PATENT ABSTRACTS OF JAPAN

(11)Publication number : **07-268634**
(43)Date of publication of application : **17.10.1995**

(51)Int.Cl. C23C 16/44
C23C 16/40
H01L 21/205

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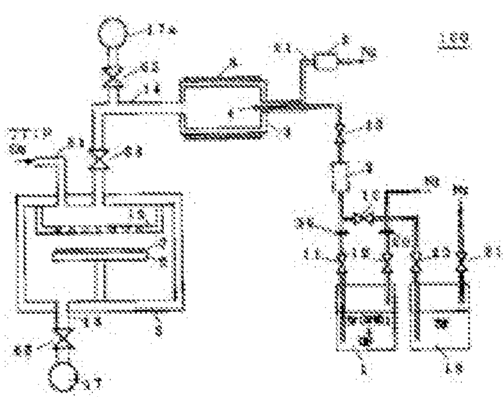
(54) CVD APPARATUS FOR LIQUID RAW MATERIAL AND CVD PROCESS USING LIUQID RAW MATERIAL AND THE LIQUID RAW MATERIAL



(57)Abstract:
PURPOSE: To obtain a CVD apparatus for a liquid raw material which prevents the trouble by particle precipitation occurring in solidification of raw material components in the transportation process, evaporation process and film forming process of the liquid raw material, a CVD process which uses the liquid raw material and is capable of forming good-quality thin films free from deviation in compsn. on a substrate and the liquid raw material.
CONSTITUTION: A piping extending from one end of valves 20 and 21 is connected to a refrigerant vessel 18 which is hermetically stored and in which a solvent (THF) is stored. The piping extending from the other end of the valve 20 is connected commonly to the piping extending from the other end of the valve 12. As a result, the cause for particles and a change (increase) in the soln. concn. by remelting of Sr(DPM)2 remaining in the pipings when the liquid raw material is freshly made to flow after the exchange of a liquid raw material container 1 are prevented and the stable supply of the raw material is executed.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]The membrane formation process in the CVD method using the CVD system for liquid materials and liquid material in which this invention forms various kinds of thin films by the CVD (chemical vapor deposition) method, It is especially related with the membrane formation process in the CVD system for liquid materials for formation of an oxide stock high permittivity thin film, and the CVD method of an oxide stock high permittivity thin film, and its liquid material about the liquid material.
[0002]
[Description of the Prior Art]In recent years, integration of semiconductor memory or a device is progressing quickly, for example, it is a rapid pace of [three years] 4 times in the number of bits in a dynamic random access memory (DRAM). This is for the purposes, such as improvement in the speed of a device, low power consumption, and low-cost-izing. However, even if it improves a degree of location, fixed capacity is required for the capacitor which is a component of DRAM, and it needs to make thickness of capacitor material thin.
[0003]However, since a limit is producing in thin film-ization in $Si\ O_2$ used until now, in order to change capacitor material and to raise a dielectric constant, the research which uses a high permittivity thin film as a capacitor material attracts attention recently.
[0004]It is most important that it is a thin film which has high permittivity as mentioned above as performance required of such a capacitor material, and that leakage current is small. That is, in the limitation using a high dielectric constant material, it is the thinnest possible film and it is necessary to make leakage current into the minimum. Generally as a desired value of an outline, it is supposed by $Si\ O_2$ conversion thickness that below 10^{-8} angstrom / cm^2 order are desirable as leakage current density at the time of 1 nm or less and 1. 65V impression.
[0005]From such a viewpoint, oxide stock dielectric films, such as tantalum oxide, lead zirconate titanate (PZT), lantern titanic acidzirconic acid lead (PLZT), strontium titanate, and barium titanate, are examined using the various forming-membranes methods.
[0006]In order to form as a thin film on the electrode for capacitors of DRAM with a level difference generally, the membrane formation using the attached CVD method with good surroundings nature to the complicated-shaped object is dramatically advantageous on a process. However, under the present circumstances, it poses a big problem that what has the evaporation characteristic stable as a raw material for CVD and good does not exist. The evaporation characteristic by heating of the dipivaloyl methane (DPM) compound of beta-diketone system currently used abundantly mainly as a raw material for CVD depends this on it not being good. Therefore, the art in which the characteristic manufactures the good dielectric membrane of fitness and manufacture nature for the fault resulting from the characteristic of a raw material is not yet established.
[0007]In the bottom of such a situation, artificers proposed the CVD material which raised volatility by leaps and bounds by dissolving in an organic solvent called a tetrahydrofuran (THF), and solution-izing the conventional solid material (application for

patent 4-252836). However, it is the former for Si O_2 film production etc. to a certain CVD system (for liquid materials) about this raw material. When it used and production of the dielectric film was tried, before arguing about the quality of membraneous quality, it turned out that a CVD system has various problems. Then, the conventional CVD system is explained first and the problem is explained below.

[0008]

The composition of conventional CVD system 2000 for liquid materials is shown in <CVD system for liquid materials of X. former> <composition of conventional CVD system for liquid materials> drawing 27. Solid Sr(DPM) $_2$ is dissolved in THF, it is considered as a liquid material, and the example which forms a strontium titanate [$SrTiO_3$] film using TTIP [Ti(O-i-C_3H_7) $_4$] and O_2 is shown. In drawing 27, the valve 10 is formed so that it may be sealed, piping which extends from the one end of the valves 11 and 12 may be connected to the liquid material container 1 in which the liquid material (here [Sr(DPM) $_2$+THF]) was stored and between the another side ends of the valves 11 and 12 may be connected. The liquid supply means 2 of a fluid massflow controller, a metering pump, etc. is connected to the another side end of the valve 11, and piping which extends from the liquid supply means 2 is connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13. The another side end of the valve 12 is connected to the nitrogen (N_2) gas supply source which is not illustrated.

[0009]The spraying nozzle 4 is arranged at the same axle in the dilution gas feed pipe 91 which has a bigger diameter than this nozzle 4, the end of the dilution gas feed pipe 91 is connected to the massflow controller 9, and the massflow controller 9 is connected to the N_2 gas supply source which is not illustrated.

[0010]The heater 8 for heating is formed in the vaporizer 3, the vaporized gas feed pipe 14 which conveys the vaporized liquid material (it is henceforth called a vaporizing raw material) to the confrontation of the spraying nozzle 4 is connected, and the vaporized gas feed pipe 14 is connected to the reaction chamber 5. In order to purge the gas in piping to the vaporized gas feed pipe 14, the purge piping 62 connected to the vacuum pump 17a is formed, and the valve 63 is formed between the vacuum pump 17a and the vaporized gas feed pipe 14. The valve 64 is formed in the reaction chamber 5 side of the vaporized gas feed pipe 14. In order to prevent the reliquefaction of vaporized gas to the vaporized gas feed pipe 14 and its peripheral equipment, the means for maintaining at an elevated temperature is added, but it omits in a figure.

[0011]The gas diffusion board 15 is arranged, the field in which the diffusion mouth of the gas diffusion board 15 was provided is countered, the heating stage 6 is formed, and the film formation substrates 7, such as silicon, are laid on this heating stage 6 so that the end connection of the vaporized gas feed pipe 14 and the introducing pipe 51 may be surrounded in the reaction chamber 5. In order to exhaust the inside of the reaction chamber 5, the exhaust line 16 connected to the vacuum pump 17 via the valve 65 is established in the reaction chamber 5. Here, although the valve 65 operates also considering the reaction chamber 5 and the vacuum pump 17 as a usual valve which severs spatial connection, it is a valve which can also change the pressure in the reaction chamber 5 arbitrarily by adjusting the degree of opening and closing of a valve.

[0012]<Operation of the conventional CVD system for liquid materials>, next figure Operation is explained referring to it. After the vaporizer 3 is heated by predetermined about 250 ** with the heater 8, a constant rate of inactive gas for dilution, for example,

N_2 gas, is supplied with the massflow controller 9, and it spouts from the spraying nozzle 4 circumference. If the valves 11, 12, and 13 are opened closing the valve 10 in this state, with the pressure of the N_2 gas supplied from the valve 12. A liquid material [Sr(DPM) $_2$+THF] is extracted from the liquid material container 1, and a stipulated amount is supplied to the vaporizer 3 by passing the liquid supply means 2.

[0013]A liquid material is an edge part at the tip of the spraying nozzle 4, by the high-speed dilution gas style which flows into the circumference, it is microatomized roughly, and carries out a distributed collision at the wide range of the wall of the vaporizer 3, and is evaporated in an instant. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14.

[0014]The TTIP raw material and oxidizing gas (O_2O etc.) which were evaporated with the bubbling apparatus which is not illustrated are given to the reaction chamber 5 via the introducing pipe 51, and are mixed with the vaporized liquid material. The uniform rate of flow distributes with the gas diffusion board 15, and mixed gas is diffused in the reaction chamber 5 maintained at the constant pressure.

[0015]The diffused mixed gas contacts the film formation substrate 7 surface heated by the heating stage 6, and forms the strontium titanate thin film by a CVD reaction. The mixed gas which did not contribute to thin film forming is discharged outside via the vacuum pump 17 from the exhaust line 16.

[0016]<the problem of the conventional CVD system for liquid materials> -- there was a problem as shown below in supply of the liquid material in the above CVD systems.

[0017](1) Although the valves 11 and 12 are closed in the case of desorption of the liquid material container 1, the valves 10 and 13 are opened and the inside of piping is purged by N_2 gas, Since the boiling point is as low as 60 ** and steam pressure is high, only THF evaporates THF used for the solvent of solid Sr(DPM) $_2$ at this time, and Sr(DPM) $_2$ which is a solid remains at ordinary temperature. Solidified Sr(DPM) $_2$ was extruded by the pressure of N_2 gas, and when it became a cause of particle or then a liquid material was poured, Sr(DPM) $_2$ which remained in piping carried out the reliquefaction of it, and it had the serious problem that solution concentration will change (increase). That is, in order that the concentration in the solution of Sr(DPM) $_2$ might change, when the heterogeneity of a film, like the presentation of the formed film shifts used as increase and a dielectric film for capacitors, it was not avoided that leakage current increases.

[0018](2), for a certain reason, the amount of supply per unit time of a liquid material comes out in small quantities dramatically, and via the liquid supply means 2, requires time for the vaporizer 3 dramatically, for raw material liquid's reaching. For example, if the piping inside diameter from the liquid supply means 2 to 0. 5 cc/min and the vaporizer 3 for the liquid material amount of supply shall be 2 mm and length shall be 300 mm, about 1 minute and 50 seconds will be taken for raw material liquid to reach even to the vaporizer 3. For this reason, a liquid material began to pass, it passed and the controllability in the end was bad, and when a flow was changed in the middle of membrane formation, adjustment of a vaporizing raw material was difficult.

[0019]Since the response of the liquid supply means 2 is still later, control the flow by opening and closing of the valve 13, but. If it is set as the value of a request of the flow rate value of the liquid supply means 2 and the valve 13 is opened, predetermined time (about 20 seconds) will flow without controlling the liquid material dammed up by the valve 13, and will reach after that the flow of the request controlled by the liquid supply

means 2. Therefore, when the valve 13 was opened at the time of the start of membrane formation, the liquid material was supplied to the vaporizer 3 in the state of overshooting, and was not able to control quantity of the vaporizing raw material. It was difficult to form membranes with accuracy sufficient on the film formation substrate 7 by the problem explained above.
[0020](3) Since the vaporizer 3 makes $Sr(DPM)_2$ evaporate and it is maintained at the elevated temperature (about 250 **), piping of the spraying nozzle 4 introduced into the vaporizer 3 and its neighborhood is also relatively high temperature (100-200 **) by heat conduction. Since it has flowed through the inside of the spraying nozzle 4 and its piping with the vaporizer, an internal pressure is low pressure like the vaporizer 3. Under such low pressure, it is very easy to evaporate the THF liquid with high steam pressure. On the other hand, since $Sr(DPM)_2$ with high steam pressure which melted into THF liquid does not evaporate, solid $Sr(DPM)_2$ remains. Therefore, the powdered sludge generated inside and there was a problem of becoming a cause of particle, or getting the inside of piping blocked in being the worst.
[0021](4) The case where some liquid materials used as the mist which floats without evaporating after spraying in the vaporizer 3 since there is a vaporizing raw material outlet towards fluid spraying are introduced into a direct reaction room, and since fluid spraying is perpendicularly made to gravity, Some liquid materials used as the mist which floats without evaporating after spraying gathered for the aliquot with gravity, and there was a problem that the temperature of a specific wall surface fell and evaporation was not performed stably.
[0022](5) The vaporizer 3 is spatially connected with the reaction chamber 5, and since it is under the same pressure, it receives the pressure fluctuation of the reaction chamber 5 directly. Since the evaporation characteristic of a liquid material is greatly influenced by the pressure, when changing the pressure in the reaction chamber 5, The equilibrium situation was torn, and since the state in the vaporizer 3 changed or the residue of the liquid material which had adhered without evaporating to the wall of the vaporizer 3 re-evaporated, there was a problem that the pressure in the reaction chamber 5 which is one of the important parameters of membrane formation by a CVD method could not be changed.
[0023](6) Even when using the liquid material which dissolved the dipivaloyl methane (DPM) compound of beta-diketone system currently used abundantly in THF liquid as a raw material for CVD, Since residue was produced in part, without the ability to evaporate thoroughly depending on the kind and manufacturing method of a raw material, since residue accumulated, with the conventional vaporizer 3, there was a problem that membranes could not be continuously formed if it takes apart and cleans periodically and a residue thing is not removed.
[0024](7) The dipivaloyl methane (DPM) compound of beta-diketone system currently used abundantly as a raw material for CVD is dramatically unstable originally, the pipeline from the vaporizer 3 to the reaction chamber 5 decomposed the part, and there was a problem constituting the membranous cause of a presentation gap and the cause of the piping blockade at the time of continuous running.
[0025](8) While the pyrolysis of the oxide stock high permittivity thin films, such as strontium titanate and barium titanate, was generally carried out and membranes had been formed, the electrical property needs to raise crystallinity by not being good and

oxidizing with oxidizing gas, such as ozone. It is more desirable to carry out this processing frequently in the middle of membrane formation. However, in the conventional device, when oxidizing gas and material gas were mixed in the field surrounded with the gas diffusion board 15 in the reaction chamber 5, there was a problem of carrying out raising dust in the field surrounded with the gas diffusion board 15.
[0026](9) Since the susceptor temperature which heats the film formation substrate 7 is usually 500-700 **, the temperature of the gas diffusion board 15 will rise by the radiation. For this reason, the trap of many will be carried out by the fine pores of the gas diffusion board 15, and the material gas with low decomposition temperature had the problem that the film formation substrate 7 could not be reached.
[0027](10) While film formation of the oxide stock high permittivity thin films, such as strontium titanate and barium titanate, had generally been carried out, since the electrical property is not good, it is necessary to raise crystallinity by carrying out high temperature processing later. It is more desirable to carry out this high temperature processing frequently in the middle of membrane formation. However, it is necessary to carry out changing to a high-temperature-processing chamber frequently and also and in the conventional method, the film formation substrate was once taken out from the reaction chamber, it was put to the atmosphere, and combined with CO_2, and there was a problem of forming barium carbonate.
[0028](11) In order that the side and the undersurface of a heater might also go up to a comparable temperature and a BST film might grow up to be the surface if wafer temperature shall be 500-700 ** when forming a BST film, when prolonged continuous running was performed, the film peeled, and there was a problem that particle occurred in the reaction chamber 5.
[0029](12) When forming a BST film continuously for a long time, a lot of residual material gas flowed into the exhaust air pump, and there was a problem that the exhaust performance of a pump fell.
[0030](13) What is known as a CVD material of metal, such as a DPM compound, or a metallic oxide, When moisture and carbon dioxide mixed in a DPM compound while accumulating into the liquid material container 1 since it deteriorated easily by mixing of moisture or carbon dioxide, there was a problem that the amount of evaporation in the vaporizer 3 decreased.
[0031]
The CVD process using the conventional liquid material is explained including the <conventional CVD process using Y. liquid material> <equipment configuration for performing a CVD process>, next the quality of membraneous quality. The liquid material which dissolved here Ba(DPM) $_2$ of the liquid material and solid which dissolved solid Sr(DPM) $_2$ in THF in THF, The example which forms a barium strontium titanate [(Ba, Sr) TiO_3] film (it is henceforth written as a BST film) using TTIP [Ti(O-i-C_3H_7) $_4$] and O_2 is shown.
[0032]The composition of CVD system 3000 for liquid materials for forming a BST film is shown in drawing 28. The liquid material [Sr(DPM) $_2$+THF] and the liquid material [Ba(DPM) $_2$+THF] are respectively stored in the liquid material container 1 and 1b.
[0033]Piping connected to the liquid material container 1b and the composition of a valve are the same as piping connected to the liquid material container 1 of conventional CVD

system 2000 for liquid materials shown in drawing 27, and the composition of a valve, and since it only changed as numerals showed below, detailed explanation is omitted. namely, the valve 11 -- the valve 12 turns into the valve 11b, the liquid supply means 2 becomes the valve 12b, and liquid supply means 2b and the valve 13 turn into the valve 13b.

[0034]The valve 13 and 13b** are connected to piping connected to the spraying nozzle 4, and via the valves 13 and 13b from the liquid material containers 1 and 1b, A liquid material [Sr(DPM) $_2$+THF] and a liquid material [Ba(DPM) $_2$+THF] are supplied, and it is mixed with dilution gas (N_2). The explanation which overlaps since other composition is the same as that of the conventional CVD system for liquid materials shown in drawing 27 is omitted.

[0035]The section composition of the BST film formed using CVD system 3000 for liquid materials of the <section composition of BST film> above is shown in drawing 29. In drawing 29, BST film L20 which the SiO_2 layer L2 was formed on Si substrate L1, and the lower Pt (platinum) electrode layer L3 was formed on it, and was formed with the CVD method on it is formed. On BST film L20, two or more upper Pt electrodes L38 for evaluating the electrical property of a BST film are formed of the sputtering technique in the size which is 1 mm in diameter.

[0036]Next, the measuring method of leakage current is explained using drawing 29. First, the voltage more than the withstand voltage of BST film L20 is impressed to the upper Pt electrode L38a which is one of the upper Pt electrodes L38, and the discharge path 99 which penetrates BST film L20 from this upper Pt electrode L38a, and reaches lower Pt electrode layer L3 is formed. Next, the upper Pt electrode L38a electrically connected with lower Pt electrode layer L3 according to the discharge path 99 is connected to earth potentials. Next, the electric capacity between the leakage current which flows between lower Pt electrode layer L3 and the upper Pt electrode L38b and lower Pt electrode layer L3, and the upper Pt electrode L38b, etc. can be measured by connecting the microammeter A to other upper Pt electrodes L38b which do not have a discharge path.

[0037]Drawing 30 is a sectional view at the time of forming membranes by using CVD system 3000 for liquid materials on the substrate L16 with a level difference which has a level difference of the aspect ratio 0.8. On the substrate L16 with a level difference, BST film L39 is formed using the DPM compound containing Ba and Sr, and TTIP and oxidizing gas (O_2 etc.).

[0038]<Membrane formation process> A membrane formation process is explained below. The substrate with which the SiO_2 layer and lower Pt electrode layer L3 were formed in order on Si substrate L1 is prepared, and BST film L20 is formed using CVD system 3000 for liquid materials shown in drawing 28 on the lower Pt electrode L3. since coverage is so good that the inside of the reaction chamber 5 at this time is under the O_2 atmosphere of pressure 10Torr and substrate temperature is low temperature, the preset temperature of the heating stage 6 is 530 ** -- under a cold condition comparatively, A liquid material flow and membrane formation time are controlled, and composition ratio (Ba+Sr)/Ti=1.0 and the BST film of 1000 A of thickness are formed by 100 A in membrane formation speed / min. BST film L39 is formed on the same conditions on the substrate L16 with a level difference shown in drawing 30.

[0039]Leakage current, electric capacity, etc. are measured by the electric circuit as

shows drawing 29 BST film L20, and oxide film conversion thickness is further measured. BST film L39 formed on the substrate L16 with a level difference is observing a section with a scanning electron microscope (SEM), and evaluation of step coverage nature is made. As shown in drawing 30, evaluation of step coverage nature sets the minimum thickness in the side of a step part to dmin, and is performed using the value of dmin /dmax by setting the maximum thickness in flat parts other than a level difference part to dmax.

[0040]It is considered by the general <problem of the CVD process using the conventional liquid material> for the membrane formation by a CVD method to have better step coverage nature compared with membrane formation by physical vapor deposition (PVD), such as weld slag. However, as shown in drawing 30, the preset temperature of the heating stage 6 shall be 550 ** on the substrate L16 with a level difference, When BST film L39 is formed, the value of dmin /dmax is 0.38 and its step coverage nature is not good as practically equal as the case where it forms with physical vapor deposition (PVD), such as weld slag. When membranes are formed on the substrate which has step shape by such step coverage nature, a presentation gap arises in the height direction of the level difference side, and, as a result, the problem that oxide film conversion thickness and leakage current increase occurs.

[0041]On the other hand, if BST film L20 is formed on lower Pt electrode layer L3 paying attention to step coverage nature being so good that substrate temperature being low temperature in the process which made preset temperature of the heating stage 6 530 **, and mentioned it above, The portion formed in early stages of the membrane formation of BST film L20 near the interface of BST film L20 and lower Pt electrode layer L3 presented the amorphous state, and this portion in early stages of membrane formation had become a factor which worsens the electrical property of whole BST film L20.

[0042]The problem of the liquid material used for the CVD process using the conventional CVD system for liquid materials and liquid material which <the problem of the liquid material used for the CVD system for Z. liquid materials and a CVD process>, next the above explained is explained. Namely, although what dissolved in an organic solvent called a tetrahydrofuran (THF), and solution-ized $Sr(DPM)_2$ which is a solid material was used as a liquid material in the CVD process using the conventional CVD system for liquid materials and liquid material, When membranes were repeatedly formed using this liquid material, vaporizer 3 inside had a problem of being easy to generate unevaporated residue. As for this, CVD materials, such as DPM compounds, such as $Ba(DPM)_2$ or $Sr(DPM)_2$, and a cyclopentadienyl compound, originate in the evaporation characteristic deteriorating easily by mixing of moisture or carbon dioxide.

[0043]Although this problem has improved by lowering the moisture concentration in a liquid material, since the hygroscopicity of the THF liquid primarily used as a solvent was high, even if it is hard to dry or performed dehydrating treatment, there was an essential problem that re-moisture absorption occurred easily.

[0044]60 ** and since [that it is low] the boiling point of THF liquid had high steam pressure, before the liquid material blew off from the nozzle 4 of the vaporizer 3, only THF evaporated it and it generated air bubbles, and when jet became intermittent, it also had the problem that the evaporation in the vaporizer 3 became intermittent.

[0045]

[Problem(s) to be Solved by the Invention]The purpose of this invention is as follows. Cancel the problem of the CVD process and liquid material using the conventional CVD system for liquid materials explained above, and a liquid material, and obtain the CVD system for liquid materials which prevented the fault by the particle deposit by solidification of a raw material component in the transport process of a liquid material, an evaporation process, and a membrane formation process.
Obtain the CVD process using the liquid material which can form a good thin film without a presentation gap on a substrate, and a liquid material.

[0046]
[Means for Solving the Problem]The CVD system for liquid materials of this invention according to claim 1, An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, Inside of said piping is washed by having further a solvent container which accommodates only said solvent liquid, and sending out said solvent to said piping from a solvent container.
[0047]The CVD system for liquid materials of this invention according to claim 2, An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, It was connected to said piping which connects said ingredient container and said vaporizer, and had further an inactive gas charging line which supplies inactive gas which raises sending-out speed of said liquid material sent out to said vaporizer from said ingredient container.
[0048]The CVD system for liquid materials of this invention according to claim 3 is attached to said inactive gas charging line, and is characterized by ****** further provided with an inactive gas cooling method for cooling inactive gas which flows through inside of said inactive gas feed pipe.
[0049]It is connected to said inactive gas charging line, and the CVD system for liquid materials of this invention according to claim 4 is further provided with a solvent container which accommodates only said solvent liquid, and sends out said solvent liquid to said inactive gas charging line.
[0050]The CVD system for liquid materials of this invention according to claim 5, An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, It was connected to said piping which connects said ingredient container and said vaporizer, was maintained at said vaporizer and power at the same pressure, and has further a receiving container in which only fixed

time accommodates said liquid material sent out from said ingredient container.
[0051]The CVD system for liquid materials of this invention according to claim 6, An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, Near [said] the vaporizer of said piping which connects said ingredient container and said vaporizer, it has a regulating valve which adjusts orifice resistance and adjusts a pressure in said piping which connects said ingredient container and said vaporizer.
[0052]The CVD system for liquid materials of this invention according to claim 7 consists of piping of said piping which connects said ingredient container and said vaporizer formed by PTFE (Poly Tetra Fluoro Ethylene) in the neighborhood of a vaporizer at least.
[0053]The CVD system for liquid materials of this invention according to claim 8 established a wrap-shaped piping cooling method for said piping near the vaporizer of said piping which connects said ingredient container and said vaporizer.
[0054]The CVD system for liquid materials of this invention according to claim 9, Said piping which connects said ingredient container and said vaporizer, and said piping which connects said reaction chamber with said vaporizer are connected to said vaporizer so that said liquid material may be given to a forward direction to gravity and said vaporized liquid material may be sent out to an opposite direction to gravity, respectively.
[0055]An inside of said vaporizer is filled up with a minute metal ball by which the temperature rise was carried out, and said liquid material contacts and evaporates the CVD system for liquid materials of this invention according to claim 10 in said minute metal ball.
[0056]The CVD system for liquid materials of this invention according to claim 11 was provided with a valve for opening sectional area adjustment to which an effective area product of said piping is changed by adjusting the degree of opening and closing of a valve near [said] the vaporizer of said piping which connects said reaction chamber with said vaporizer.
[0057]The CVD system for liquid materials of this invention according to claim 12, Said reaction chamber mixes said vaporized liquid material and said reactant gas, is provided with a gas diffusion board uniformly diffused in said reaction chamber, and keeps temperature of said gas diffusion board constant by a cooling method provided in a field to which said gas diffusion board of a wall of said reaction chamber contacts.
[0058]The CVD system for liquid materials of this invention according to claim 13, Said reaction chamber lays a substrate with which said thin film layer is formed, is provided with susceptor which heats this substrate, and said susceptor, A heating element used as a heat source, and a conductor which tells heat from said heating element to said substrate by heat conduction, It has said heating element, a supporter which accommodates said conductor, and a heat-insulating element which is provided in the circumference of said heating element and said conductor, and insulates said supporter, and said heating element and said conductor, and is constituted.
[0059]A CVD system for liquid materials of ******14** of this invention, Equip the

exterior of a reaction chamber with an exhaust means for exhausting said vaporized liquid material and said reactant gas, and between said exhaust means and said reaction chamber, It has a gas adsorption means to cool, to adsorb said vaporized liquid material and said reactant gas, and to prevent said liquid material and said reactant gas from reaching said exhaust means.
[0060]The CVD system for liquid materials of this invention according to claim 15, It has a reaction chamber which forms a thin film layer using an ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, said vaporized liquid material, and a reactant gas, and said vaporizer and said reaction chamber are formed by integral construction.
[0061]This invention is characterized by the CVD system for liquid materials according to claim 16 comprising the following.
A feeding hole which said reaction chamber is provided with a gas diffusion board which diffuses said vaporized liquid material uniformly in said reaction chamber, and said gas diffusion board makes pass said said vaporized liquid material.
Reactive gas feed holes connected to a supply source of said reactive gas.

[0062]Said reaction chamber lays a substrate with which said thin film layer is formed, the CVD system for liquid materials of this invention according to claim 17 is provided with susceptor which heats this board, and said susceptor has a lamp heater as a heat source.
[0063]The CVD system for liquid materials of this invention according to claim 18 established a dehydration means into said ingredient container.
[0064]A CVD process using the liquid material of this invention according to claim 19, A vaporizing raw material which made a liquid material which dissolved a solid state DPM system organic metallic compound which are Ba and Sr raw material in an organic solvent heat and evaporate, A thing which made a liquid organic metallic compound which is Ti raw material evaporate is mixed, chemical vapor deposition (Chemical Vapor Deposition : omit the following CVD) which makes it react to O_2 which is an oxidizer, and forms a thin film layer on a substrate -- law () [Ba and] Sr) In a CVD process which forms a TiO_3 (it omits the following BST) film, N_2O is also added as an oxidizer in addition to O_2.
[0065]A CVD process using the liquid material of this invention according to claim 20, A vaporizing raw material which made a liquid material which dissolved a solid state DPM system organic metallic compound which are Ba and Sr raw material in an organic solvent heat and evaporate, In a CVD process which forms a BST film with a CVD method which mixes a thing which made a liquid organic metallic compound which is Ti raw material evaporate, introduces into a reaction chamber, and carries out a chemical reaction to an oxidizer there, and which is made to vapor-deposit on a substrate, A process of performing predetermined processing to said initial film in order to crystallize said initial film which is easy to make membrane formation of said BST film amorphous with a formation process of an initial film which is a film in early stages of membrane formation, A CVD process using a liquid material considering it as gradual membrane formation performed by dividing into a process of forming a latter-part film on said initial film.

[0066]As for said predetermined processing, a CVD process using the liquid material of this invention according to claim 21 performs lamp annealing processing after said initial film formation.
[0067]Said predetermined processing of a CVD process using the liquid material of this invention according to claim 22 forms ST film as said initial film.
[0068]A CVD process using the liquid material of this invention according to claim 23 performs O_3 processing in which said predetermined processing puts said initial film to O_3 gas after said initial film formation.
[0069]A CVD process using the liquid material of this invention according to claim 24 performs O_2 plasma treatment to which said predetermined processing puts said initial film to O_2 plasma after said initial film formation.
[0070]It gives mechanical polish (ChemicalMechanical Polishing) to said substrate in order to remove a foreign matter on said substrate, before a CVD process using the liquid material of this invention according to claim 25 forms membranes on said substrate.
[0071]It performs washing processing by HF (fluoric acid) to said substrate in order to remove a foreign matter on said substrate, before a CVD process using the liquid material of this invention according to claim 26 forms membranes on said substrate.
[0072]A CVD process using the liquid material of this invention according to claim 27 low-temperature-ized temperature of said substrate, and raised step coverage nature.
[0073]A CVD process using the liquid material of this invention according to claim 28 supplies supply of a liquid organic metallic compound which is said Ti raw material from a liquid material which dissolved a solid state DPM system organic metallic compound in an organic solvent.
[0074]In a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent, a solvent which contains a ligand of this organic metallic compound in the part is used for a liquid material for the CVD of this invention according to claim 29.
[0075]A liquid material for CVD, wherein tetrahydropyran is used for a liquid material for the CVD of this invention according to claim 30 as this solvent in a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent.
[0076]In a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent, dioxane was used for a liquid material for the CVD of this invention according to claim 31 as this solvent.
[0077]A liquid material for CVD, wherein a nonpolar molecule solvent is used for a liquid material for the CVD of this invention according to claim 32 as this solvent in a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent.
[0078]
[Function]According to the CVD system for liquid materials of this invention according to claim 1, the inside of piping can be washed by sending out a solvent to said piping from a solvent container.
[0079]According to the CVD system for liquid materials of this invention according to claim 2, the sending-out speed of the liquid material sent out to a vaporizer from an ingredient container can be raised by having had the inactive gas charging line.
[0080]According to the CVD system for liquid materials of this invention according to claim 3, the inactive gas which flows through the inside of an inactive gas feed pipe can

be cooled by having had the inactive gas cooling method further.
[0081]According to the CVD system for liquid materials of this invention according to claim 4, solvent liquid can be sent out to an inactive gas charging line because it can have further a solvent container which accommodates only solvent liquid.
[0082]Since it has a receiving container in which only fixed time accommodates a liquid material according to the CVD system for liquid materials of this invention according to claim 5, flow control of a liquid material can be performed.
[0083]Since it has the regulating valve which adjusts the pressure in piping according to the CVD system for liquid materials of this invention according to claim 6, the evaporation characteristic of the liquid material influenced by the pressure in piping is controllable.
[0084]According to the CVD system for liquid materials of this invention according to claim 7, the residue of a liquid material can be prevented from reducing heat conduction and being accumulated into piping by the thing of piping for which the neighborhood of a vaporizer is formed by PTFE at least.
[0085]According to the CVD system for liquid materials of this invention according to claim 8, residue can be prevented from reducing the rise in heat of piping, and a liquid material evaporating within piping, and being accumulated by having established the wrap-shaped piping cooling method for piping near the vaporizer of piping.
[0086]Since according to the CVD system for liquid materials of this invention according to claim 9 a liquid material is given to a forward direction to gravity and the vaporized liquid material is sent out to an opposite direction to gravity, the residue of a liquid material can be prevented from being accumulated into a vaporizer.
[0087]Since it fills up with the minute metal ball by which the temperature rise was carried out to the inside of a vaporizer according to the CVD system for liquid materials of this invention according to claim 10, a liquid material can contact and evaporate in a minute metal ball.
[0088]According to the CVD system for liquid materials of this invention according to claim 11, near the vaporizer, the degree of opening and closing of a valve can be adjusted, the effective area product of piping can be changed, and the pressure in a vaporizer can be kept independent of a reaction chamber by having had the valve for opening sectional area adjustment.
[0089]According to the CVD system for liquid materials of this invention according to claim 12, the temperature of a gas diffusion board can be kept constant by cooling a gas diffusion board by the cooling method provided in the field to which a gas diffusion board contacts.
[0090]Since the heating element and the conductor are insulated by the heat-insulating element to the supporter in susceptor according to the CVD system for liquid materials of this invention according to claim 13, a supporter is prevented from being heated.
[0091]Since the exhaust means is provided with the gas adsorption means according to the CVD system for liquid materials of this invention according to claim 14, a liquid material and a reactant gas can be prevented from reaching an exhaust means.
[0092]Since the vaporizer and the reaction chamber are formed by integral construction according to the CVD system for liquid materials of this invention according to claim 15, transportation of the vaporized liquid material to a reaction chamber from a vaporizer is performed efficiently.

[0093]According to the CVD system for liquid materials of this invention according to claim 16, a gas diffusion board is having a feeding hole which passes the vaporized liquid material, and the reactive gas feed holes connected to the supply source of reactive gas, and a liquid material and reactive gas can be prevented from blending superfluously.
[0094]According to the CVD system for liquid materials of this invention according to claim 17, annealing treatment is possible, without taking out a substrate because susceptor has a lamp heater as a heat source.
[0095]According to the CVD system for liquid materials of this invention according to claim 18, degradation of the liquid material by moisture mixing in a liquid material can be prevented by having established the dehydration means into the ingredient container.
[0096]According to the CVD process using the liquid material of this invention according to claim 19, the membraneous quality of a BST film can be improved by adding N_2O as an oxidizer in addition to O_2.
[0097]According to the CVD process using the liquid material of this invention according to claim 20, by forming a BST film gradually and performing predetermined processing to an initial film, the initial film which is easy to make it amorphous can be crystallized, and the membraneous quality of a BST film can be improved.
[0098]As predetermined processing, by performing lamp annealing processing, the initial film which is easy to make it amorphous can be crystallized, and, according to the CVD process using the liquid material of this invention according to claim 21, the membraneous quality of a BST film can be improved after initial film formation.
[0099]According to the CVD process using the liquid material of this invention according to claim 22, the membraneous quality of a BST film can be improved by forming ST film as an initial film.
[0100]After initial film formation, by performing O_3 processing, the initial film which is easy to make it amorphous can be crystallized, and, according to the CVD process using the liquid material of this invention according to claim 23, the membraneous quality of a BST film can be improved.
[0101]After initial film formation, by performing O_2 plasma treatment, the initial film which is easy to make it amorphous can be crystallized, and, according to the CVD process using the liquid material of this invention according to claim 24, the membraneous quality of a BST film can be improved.
[0102]According to the CVD process using the liquid material of this invention according to claim 25, by giving mechanical polish to a substrate, the foreign matter on a substrate can be removed and membraneous quality can be improved.
[0103]According to the CVD process using the liquid material of this invention according to claim 26, by performing washing processing by HF to a substrate, the foreign matter on a substrate can be removed and membraneous quality can be improved.
[0104]According to the CVD process using the liquid material of this invention according to claim 27, step coverage nature improves by low-temperature-izing temperature of a substrate.
[0105]According to the CVD process using the liquid material of this invention according to claim 28, the membraneous quality of a BST film can be improved by supplying supply of the liquid organic metallic compound which is Ti raw material from the liquid material which dissolved the solid state DPM system organic metallic compound in the organic solvent.

[0106]According to the liquid material for the CVD of this invention according to claim 29, the evaporation characteristic of a liquid material can be improved by using the solvent which contains the ligand of an organic metallic compound in the part.
[0107]According to the liquid material for the CVD of this invention according to claim 30, the evaporation characteristic of a liquid material can be improved by having used tetrahydropyran as a solvent.
[0108]According to the liquid material for the CVD of this invention according to claim 31, the evaporation characteristic of a liquid material can be improved by having used dioxane as a solvent.
[0109]According to the liquid material for the CVD of this invention according to claim 32, the evaporation characteristic of a liquid material can be improved by using a nonpolar molecule solvent as a solvent.
[0110]
[Example]
<working example of the CVD system for A. liquid materials> -- working example of the CVD system for liquid materials by this invention is first described using drawing 1 - drawing 16. A liquid material dissolves $Sr(DPM)_2$ which is a solid material in the THF (tetrahydrofuran) liquid which is a solvent, and the example which forms strontium titanate [$SrTiO_3$] using TTIP [$Ti(O\text{-}i\text{-}C_3H_7)_4$] and O_2 is shown. The part which overlaps with a Prior art omits the explanation suitably. Distinguish the context of arrangement of a valve etc. by the direction into which a fluid and a gas flow for convenience, the side by which a fluid and a gas flow into a figure is called the upstream, and the side flowing out is called the downstream.
[0111]<A1. working example 1> <equipment configuration of working example 1> drawing 1 is a schematic diagram showing CVD system 100 for liquid materials by working example 1 of this invention. In drawing 1, the valve 10 is formed so that it may be sealed, piping which extends from the one end of the valves 11 and 12 may be connected to the liquid material container 1 in which the liquid material (here [$Sr(DPM)_2$+THF]) was stored and between the another side ends of the valves 11 and 12 may be connected. It is sealed, piping which extends from the one end of the valves 20 and 21 is connected to the solvent container 18 in which the solvent (here THF) was stored, and piping which extends from the another side end of the valve 20 is connected common to piping which extends from the another side end of the valve 12. And piping which extends from the one end of the valve 19 is connected to piping in which piping which extends from the another side end of the valve 20 extends from the another side end of the valve 12 in common. The nitrogen (N_2) gas supply source which is not illustrated is connected to the another side end of the valve 19 and the valve 21, and a liquid material and a solvent are sent out in piping by applying the pressure by nitrogen gas to the liquid material container 1 and the solvent container 18 (fed).
[0112]The terminal areas 39 and 40 for connecting to the pipe line the liquid material container 1 which contains the valves 11 and 12, respectively are established in piping which extends from the another side end of the valves 11 and 12. In addition, since the composition after the liquid supply means 2 is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0113]Operation is explained referring to <operation of the CVD system of working

example 1>, next drawing 1. In the usual membrane formation, the vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of inactive gas for dilution is supplied with the massflow controller 9, and dilution gas is made to blow off from the spraying nozzle 4 circumference. The valves 11, 12, and 19 are opened and the valves 10, 13, 20, and 21 are closed. Next, if the valve 13 is opened and a constant rate of liquid materials [Sr(DPM) $_2$+THF] are supplied from the liquid supply means 2, by the edge part at the tip of the spraying nozzle 4, by the surrounding high-speed dilution gas style, it will be microatomized roughly, and a liquid material will carry out a distributed collision at the wide range of the wall of the vaporizer 3, and will be evaporated in an instant.

[0114]The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14, Like conventional CVD system 2000 for liquid materials shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.

[0115]When the liquid materials [Sr(DPM) $_2$+THF] in the liquid material container 1 decrease in number and it exchanges, the valves 11, 12, and 19 are closed first, the valves 13, 10, 20, and 21 are opened and THF liquid is poured in piping in the course through the valves 20, 10, and 13 from the solvent container 18 for washing. THF liquid is poured for a while, and after removing thoroughly the Sr(DPM) $_2$ ingredient which remains in piping, the inside of piping is purged by N_2 gas by closing the valves 20 and 21 and opening the valve 19. At this time, the solution and N_2 gas by which Sr(DPM) $_2$ which remains melted into THF liquid are exhausted from the vacuum pump 17a via the purge piping 62 provided in the vaporized gas feed pipe 14. In purging, the valve 64 provided in the reaction chamber 5 side of the vaporized gas feed pipe 14 is closed, and it opens the valve 63 provided between the vacuum pump 17a and the vaporized gas feed pipe 14.

[0116]Thus, after washing the inside of piping thoroughly, in the terminal areas 39 and 40, connection of the liquid material container 1 containing the valves 11 and 12 is refused, and the liquid material container 1 is removed.

[0117]As beyond the <a characteristic operation and effect of working example 1> explained, the CVD system concerning working example 1 of this invention, It has the solvent container 18 for pipe washing, and the penetrant remover supply line from the solvent container 18 is connected to the preceding paragraph of the valve 10 which is a purge-gas-feed mouth of the liquid material container 1 in common, and after removing the liquid and solid ****** in piping thoroughly by pouring a penetrant remover, the liquid material container 1 is exchangeable. Therefore, when it becomes a cause of particle or a liquid material is newly poured after exchange of the liquid material container 1, solution concentration is prevented from Sr(DPM) $_2$ which remained in piping remelting, and changing (increase), and stable feeding can be performed.

[0118]<A2. working example 2> <equipment configuration of working example 2> drawing 2 is a schematic diagram showing CVD system 200 for liquid materials by working example 2 of this invention. In drawing 2, it extends from the liquid supply means 2, and multipoint connection of the dilution gas feed pipe 92 is carried out to piping connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13 via the valve 22 at the downstream of the valve 13. The end of the dilution gas feed pipe 92 is connected to the N_2 gas supply source which is not illustrated via the massflow controller

24, and the heat exchanger 23 for cooling is formed in the circumference of the dilution gas feed pipe 92 between the massflow controller 24 and the valve 22. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0119]<Operation of the CVD system of working example 2>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of inactive gas for dilution (here N_2) is supplied with the massflow controller 9 and the massflow controller 24, and dilution gas is spouted from the spraying nozzle 4 and its circumference. The valves 10, 11, 12, and 13 are closed at this time.
[0120]Next, if the valves 11, 12, and 13 are opened with the valve 10 closed, a constant rate of liquid materials [Sr(DPM) $_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. It is mixed with the dilution gas supplied from the dilution gas feed pipe 92, and the liquid material which passed the valve 13 is sent into the vaporizer 3.
[0121]Since it is cooled by the heat exchanger 23 for cooling and dilution gas is given, a liquid material is not evaporated in the middle of piping, but blows off from the spraying nozzle 4 as a vapor-liquid mixture, and is evaporated on the vaporizer wall surface maintained at the elevated temperature.
[0122]The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14, Like the conventional CVD system for liquid materials shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.
[0123]If the piping inside diameter from the liquid supply means 2 to 0. 5 cc/min and the vaporizer 3 for the liquid material amount of supply will be 2 mm, for example if even a vaporizer feeds a liquid material like before with a fluid, and length shall be 300 mm, will require for a liquid material reaching even to the vaporizer 3 for about 1 minute and 50 seconds, but. According to this invention, the rate of flow of the vapor-liquid mixture obtained by supplying the dilution gas of 200 cc/min becomes very quick, and reaches the vaporizer 3 in about 0.28 seconds. For this reason, also when a liquid material began to pass, it passes, and the controllability in the end has been improved and a flow is changed in the middle of membrane formation, adjustment of the amount of vaporizing raw materials becomes easy.
[0124]As beyond the <a characteristic operation and effect of working example 2> explained, the CVD system concerning working example 2 of this invention, Since piping which extends from the liquid supply means 2 and is connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13 is further equipped with the dilution gas feed pipe 92 which has the heat exchanger 23 for cooling, By mixing with the cooled dilution gas, the liquid material prevented evaporating within piping, and the rate of flow of the liquid material of the vapor-liquid mixed state was sped up, a liquid material began to pass, it passed and the controllability in the end has been improved.
[0125]Although <the modification of working example 2>, in addition above-mentioned working example 2 showed the example of membrane formation by one kind of liquid material, even if a liquid material is plurality, the equipment configuration of working example 2 is applicable. CVD system 200a for liquid materials in the case of supplying

two or more liquid materials is shown in drawing 3.
[0126]CVD system 200a for liquid materials shown in drawing 3 is a device for forming a BST film, A liquid material [Sr(DPM) $_2$+THF] and a liquid material [Ba(DPM) $_2$+THF] are respectively stored in the liquid material container 1 and 1a, and the THF liquid which is a solvent is stored in the solvent container 18.
[0127]Piping connected to the liquid material container 1a and the solvent container 18a and the composition of a valve are figures. It is the same as that of shown conventional CVD system 2000 for liquid materials, and since it only changed as numerals showed below, detailed explanation is omitted. namely, the valve 11 -- the valves 11a and 11b -- the valve 12 turns into the valves 12a and 12b, the liquid supply means 2 becomes the liquid supply means 2a and 2b, and the valve 13 turns into the valves 13a and 13b.
[0128]The valves 13, 13a, and 13b are connected to piping connected to the spraying nozzle 4, and via the valves 13 and 13a from the liquid material containers 1 and 1a, A liquid material [Sr(DPM) $_2$+THF] and a liquid material [Ba(DPM) $_2$+THF] are supplied, and from the solvent container 18b, THF liquid is supplied and it is mixed with dilution gas (N_2).
[0129]The THF liquid whose mixed order is a solvent first is mixed with dilution gas (N_2), and, subsequently to order, a liquid material [Sr(DPM) $_2$+THF] and a liquid material [Ba(DPM) $_2$+THF] are mixed. By mixing with the first THF liquid, since the THF liquid more than maximum vapor tension is added by N_2 gas, In the case of mixing with a liquid material [Sr(DPM) $_2$+THF] and a liquid material [Ba(DPM) $_2$+THF], the deposit of Ba(DPM) $_2$ of an individual or Sr(DPM) $_2$ by THF liquid evaporating is not generated.
[0130]Although the spraying nozzle 4 has been arranged like the conventional CVD system for liquid materials at the same axle in the bigger dilution gas feed pipe 91 than this nozzle 4 and it was considered as the structure of passing dilution gas from the circumference of the spraying nozzle 4, in above-mentioned working example 2 and its modification, In order to supply dilution gas also from the same piping as the spraying nozzle 4, it is good also as composition which excludes the dilution gas supply system which stands in a row in the dilution gas feed pipe 91 and it.
<A3. working example 3> <equipment configuration of working example 3> drawing 4 is a schematic diagram showing CVD system 300 for liquid materials by working example 3 of this invention. In drawing 4, the valve 13 is formed in a part for the direct anterior part of the spraying nozzle 4 of the vaporizer 3, Apart from the supply line of the liquid material from the former, a branch line is established in the upstream of the valve 13 via the valve 26, the one end is connected to the vaporizer 3 and the liquid pool tank 25 maintained at power at the same pressure, and the vacuum pump 17b is connected to the liquid pool tank 25. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0131]<Operation of the CVD system of working example 3>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. In this state, the valves 10, 11, 12, 13, and 26 are closed.
[0132]After exhausting the inside of the liquid pool tank 25 with the vacuum pump 17b

first and making it power at the same pressure in the vaporizer 3 in membrane formation, the valve 26 is opened, subsequently the valves 11 and 12 are opened, and the liquid material supplied via the liquid supply means 2 from the liquid material container 1 is discharged on the liquid pool tank 25. At this time, since there is a pressure differential in the liquid pool tank 25 in piping, a liquid material flows into the liquid pool tank 25 in the state of overshooting. If the liquid material through put of the liquid supply means 2 is stabilized, the valve 26 will be closed at the same time it opens the valve 13, and a liquid material will be supplied in the vaporizer 3. The liquid supply means 2 with a late response can also keep the quantity of the liquid material to evaporate constant for a change in the space where the pressure was kept the same, without making the flow of a liquid material overshoot. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14, Like the conventional CVD system for liquid materials shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.
[0133]As beyond the <a characteristic operation and effect of working example 3> explained, the CVD system concerning working example 3 of this invention, The branch line was established in the spraying nozzle direct anterior part of the vaporizer, one side was connected to the vaporizer and the liquid pool tank maintained at power at the same pressure, since the valve which changes the flow direction of liquid to a vaporizer and a liquid pool tank was provided, it cannot be influenced by the speed of response of a liquid supply means, but the vaporizing raw material could be controlled with sufficient accuracy.
[0134]<A4. working example 4> <equipment configuration of working example 4> drawing 5 is a schematic diagram showing CVD400 device for liquid materials by working example 4 of this invention. Piping and the nozzle which extend from the liquid supply means 2 and are connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13 in drawing 5, It comprises the Teflon small tube 27 really formed by PTFE (it is called Teflon after Poly Tetra Fluoro Ethylene :) which is a polymer material. Since other composition is the same as that of the conventional CVD system for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0135]<Operation of the CVD system of working example 4>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. The valves 10, 11, 12, and 13 are closed in this state.
[0136]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [$Sr(DPM)_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. Since piping and the spraying nozzle 4 which extend from the liquid supply means 2 and are connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13 really comprise the small tube 27 made from Teflon with small thermal conductivity as a thing, The heat from the vaporizer 3 currently maintained at the elevated temperature (about 250 **) is not transmitted easily, and the small tube 27 made from Teflon is maintained at low temperature (50-100 **).
[0137]For this reason, THF liquid with high steam pressure is also hard to be evaporated in the small tube 27 made from Teflon, since it is smooth in an internal surface, the

$Sr(DPM)_2$ ingredient of a liquid material is prevented from adhering to an internal surface as residue, and all the liquid materials are introduced in the vaporizer 3. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14, Like the conventional CVD system for liquid materials shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.

[0138]As beyond the <a characteristic operation and effect of working example 4> explained, the CVD system concerning working example 4 of this invention, Since piping and the spraying nozzle 4 which are connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13 are really constituted from the small tube 27 made from Teflon with small thermal conductivity as a thing, By the adiathermancy of the small tube 27 made from Teflon, and the smooth nature of the surface in the small tube 27 made from Teflon, generating and adhesion of a residue thing of a liquid material in piping are prevented, and supply of the stable liquid material can be realized.

[0139]<A5. working example 5> <equipment configuration of working example 5> drawing 6 is a schematic diagram showing CVD system 500 for liquid materials by working example 5 of this invention. In drawing 6, it extends from the liquid supply means 2, and the water cooled jacket 28 is formed in the surroundings of piping near the induction to the vaporizer 3 of piping connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13. The water cooled jacket 28 is for cooling the heat transmitted from the vaporizer 3 by heat conduction, and is stuck and provided in piping. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.

[0140]<Operation of the CVD system of working example 5>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. The valves 10, 11, 12, and 13 are closed in this state.

[0141]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [$Sr(DPM)_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. Extend from the liquid supply means 2 and the water cooled jacket 28 is formed in the surroundings of piping connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13, The heat from the vaporizer 3 maintained at the elevated temperature can be prevented from getting across to piping by heat conduction, and the liquid material which flows through the inside of a pipe can be maintained at low temperature.

[0142]For this reason, THF liquid with high steam pressure is also hard to be evaporated, the $Sr(DPM)_2$ ingredient of a liquid material is prevented from serving as residue, and all the liquid materials are introduced in the vaporizer 3. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14, Like conventional CVD system 2000 for liquid materials shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.

[0143]As beyond the <a characteristic operation and effect of working example 5>

explained, CVD system 500 for liquid materials concerning working example 5 of this invention, By forming the water cooled jacket 28 in the surroundings of piping connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13, The heat from the vaporizer 3 is prevented from getting across to piping by heat conduction, since the liquid material which flows through the inside of a pipe can be maintained at low temperature, generating of the residue thing of the liquid material in piping is prevented, and supply of the stable liquid material can be realized.

[0144]<A6. working example 6> <equipment configuration of working example 6> drawing 7 is a schematic diagram showing CVD system 600 for liquid materials by working example 6 of this invention. In drawing 7, it extends from the liquid supply means 2, and the needle valve 29 which can adjust orifice resistance is formed near the induction to the vaporizer 3 of piping connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13. The tip of the valve shaft is needlelike and the needle valve 29 is a valve from which orifice resistance changes with the fit condition to the hole of conical shape delicately. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.

[0145]<Operation of the CVD system of working example 6>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. The valves 10, 11, 12, and 13 are closed in this state.

[0146]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [Sr(DPM) $_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. Since the needle valve 29 is formed near the induction to the vaporizer 3 of piping which extends from the liquid supply means 2 and is connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13, By operating the needle valve 29 and adjusting the degree of opening and closing, the pressure in upstream piping can be kept higher than the pressure in the vaporizer 3 from the needle valve 29.

[0147]For this reason, THF liquid with high steam pressure is also hard to be evaporated, the Sr(DPM) $_2$ ingredient of a liquid material is prevented from serving as residue, and all the liquid materials are introduced in the vaporizer 3. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14, Figure Like the shown conventional CVD system for liquid materials, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.

[0148]As beyond the <a characteristic operation and effect of working example 6> explained, CVD system 600 for liquid materials concerning working example 6 of this invention, By adjusting the degree of opening and closing of the needle valve 29 provided near the induction to the vaporizer 3 of piping connected to the spraying nozzle 4 of the vaporizer 3 via the valve 13, Since the pressure in upstream piping can be kept higher than the pressure in the vaporizer 3 from the needle valve 29, generating of the residue thing of the liquid material in piping is prevented, and supply of the stable liquid material can be realized.

[0149]<A7. working example 7> <equipment configuration of working example 7>

drawing 8 is a schematic diagram showing CVD system 700 for liquid materials by working example 7 of this invention. In drawing 8, piping which extends from the liquid supply means 2 is connected to the spraying nozzle 4a of the vaporizer 3a via the valve 13. The spraying nozzle 4a is arranged at the same axle in the dilution gas feed pipe 91a which has a bigger diameter than this nozzle 4a, and the spraying nozzle 4a and the dilution gas feed pipe 91a, It is arranged so that a liquid material and dilution gas may blow off to perpendicular down [of the vaporizer 3a] (it is a forward direction to gravity), and the vaporized gas feed pipe 14a is arranged so that a vaporizing raw material may be sent out to perpendicular above [of the vaporizer 3a] (it is an opposite direction to gravity). Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.

[0150]<Operation of the CVD system of working example 7>, next operation are explained. The vaporizer 3a is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4a. The valves 10, 11, 12, and 13 are closed in this state.

[0151]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [$Sr(DPM)_2$+THF] will be sent out towards the vaporizer 3a from the liquid supply means 2. The liquid material which reached the vaporizer 3a falls being roughly microatomized by the high-speed dilution gas style which flows into the circumference at the tip of the spraying nozzle 4a, and spreading in the vaporizer 3a by it, carries out a distributed collision at the wide range of the wall of the vaporizer 3a, and is evaporated in an instant. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14a.

[0152]Thus, the spraying nozzle 4a and the dilution gas feed pipe 91a, Since it is arranged so that a liquid material and dilution gas may blow off to perpendicular down [of the vaporizer 3a] (it is a forward direction to gravity), the microatomized liquid material will have a perpendicular down (it is a forward direction to gravity) velocity component conjointly with fall by prudence.

[0153]On the other hand, since the vaporized gas feed pipe 14a is arranged so that a vaporizing raw material may be sent out to perpendicular above [of the vaporizer 3a] (it is an opposite direction to gravity), even when a liquid material is not evaporated, the liquid material of a mist state is prevented from being conveyed to the reaction chamber 5. The vaporized liquid material is conveyed to the reaction chamber 5 side by the pressure differential through the vaporized gas feed pipe 14a, Like conventional CVD system 2000 for liquid materials shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.

[0154]As beyond the <a characteristic operation and effect of working example 7> explained, CVD system 700 for liquid materials concerning working example 7 of this invention, The spraying nozzle 4a and the dilution gas feed pipe 91a are arranged so that a liquid material and dilution gas may blow off to perpendicular down [of the vaporizer 3a] (it is a forward direction to gravity), Since the vaporized gas feed pipe 14a is arranged so that a vaporizing raw material may be sent out to perpendicular above [of the

vaporizer 3a] (it is an opposite direction to gravity), the liquid material of a mist state is prevented from being conveyed to the reaction chamber 5.
[0155]<A8. working example 8> <equipment configuration of working example 8> drawing 9 is a schematic diagram showing CVD system 800 for liquid materials by working example 7 of this invention. In drawing 9, to the vaporized gas feed pipe 14 which connects the reaction chamber 5 with the vaporizer 3. The effective area product of the vaporized gas feed pipe 14 is changed near the vaporizer 3, conductance is changed, the flow of the gas containing the vaporizing raw material conveyed to the reaction chamber 5 from the vaporizer 3 is adjusted, and the conductance valve 30 for keeping independent respectively the internal pressure of the vaporizer 3 and the reaction chamber 5 is formed. Internal pressure is measured to the vaporizer 3, the measurement value is changed into an electrical signal, and the pressure gauge 34 outputted as a pressure signal is formed.
[0156]Although the conductance valve 30 can just change the effective area product of the vaporized gas feed pipe 14 and can take various composition for that purpose, it shows the following composition as an example here. Namely, the opening and closing plate 31 of the size [conductance valve / 30] according to the effective area of the vaporized gas feed pipe 14, The driving shaft 32 which is connected to the opening and closing plate 31, and drives the opening and closing plate 31 to the diameter direction of the effective area of the vaporized gas feed pipe 14, It has the driving source 33 which operates the driving shaft 32, and has the composition of changing the effective area product of the vaporized gas feed pipe 14, by driving to a diameter direction so that the opening and closing plate 31 may close the effective area of the vaporized gas feed pipe 14. Here, since the gas which includes in the opening and closing plate 31 the vaporizing raw material by which the temperature rise was carried out with the vaporizer 3 contacts, it will be in a high temperature state comparable as this gas at least. On the other hand, since the driving source 33 has the electrical and electric equipment and electronic parts, it is necessary to prevent being in a high temperature state, therefore the driving shaft 32 has a thermal protection structure or a cooler style. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0157]<Operation of the CVD system of working example 8>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. The valves 10, 11, 12, and 13 are closed in this state.
[0158]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [Sr(DPM) $_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. At the tip of the spraying nozzle 4, by the high-speed dilution gas style which flows into the circumference, it is microatomized roughly, and the liquid material which reached the vaporizer 3 carries out a distributed collision at the wide range of the wall of the vaporizer 3, and is evaporated in an instant. At this time, the pressure in the vaporizer 3 is measured by the pressure gauge 34.
[0159]Usually, when it does not have the conductance valve 30, or in not making it operate conductance valve 30, the internal pressure of the vaporizer 3 is interlocked with the internal pressure of the reaction chamber 5, and changes. In membrane formation by a

CVD method, the pressure in the reaction chamber 5 is one of the important parameters, and the pressure in the reaction chamber 5 may be variously changed in the process of membrane formation. On the other hand, when it is greatly influenced by the internal pressure of the vaporizer 3, the internal pressure of the reaction chamber 5 is interlocked with and the internal pressure of the vaporizer 3 changes, the evaporation characteristic of a liquid material, The amount of evaporation of a liquid material decreases, or the residue of the liquid material which had adhered without evaporating to the wall of the vaporizer 3 conversely re-evaporates, the amount of evaporation of a liquid material increases, and a vaporizing raw material is no longer stably supplied to the reaction chamber 5.
[0160]Here, a change of the pressure in the reaction chamber 5 is made by changing the degree of opening and closing of the valve 65 provided in the preceding paragraph of the vacuum pump 17. therefore, in enlarging an opening for the valve 65 and making internal pressure of the reaction chamber (namely, -- increasing displacement) 5 into low pressure. The opening and closing plate 31 of the conductance valve 30 is made to drive so that the gas which includes a vaporizing raw material from the vaporizer 3 may not be conveyed too much, and the effective area of the vaporized gas feed pipe 14 may be closed, The effective area product of the vaporized gas feed pipe 14 is made small, the flow of the gas containing the vaporizing raw material conveyed to the reaction chamber 5 is decreased, and the internal pressure of the vaporizer 3 is kept constant.
[0161]in making an opening small for the valve 65 conversely and making internal pressure of the reaction chamber (namely, -- reducing displacement) 5 into high voltage, In order to promote transportation of the gas which includes a vaporizing raw material from the vaporizer 3, the opening and closing plate 31 of the conductance valve 30 is made to drive so that the effective area of the vaporized gas feed pipe 14 may be opened, Enlarge the effective area product of the vaporized gas feed pipe 14, the flow of the gas containing the vaporizing raw material conveyed to the reaction chamber 5 is made to increase, and the internal pressure of the vaporizer 3 is kept constant. However, internal pressure of the reaction chamber 5 is not made higher than the internal pressure of the vaporizer 3, and a vaporizing raw material certainly flows toward the reaction chamber 5 from the vaporizer 3.
[0162]Although the pressure gauge 34 which provided opening and closing of the conductance valve 30 in the vaporizer 3 is controlled based on the pressure signal which measures change of a pressure and is outputted, since the relation of this invention is [control mechanisms for it] thin, detailed explanation is omitted.
[0163]Thus, the liquid material evaporated by being stabilized under the constant pressure, Like conventional CVD system 2000 for liquid materials which it was conveyed to the reaction chamber 5 side through the vaporized gas feed pipe 14 according to the pressure differential, and was shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.
[0164]As beyond the <a characteristic operation and effect of working example 8> explained, CVD system 800 for liquid materials concerning working example 8 of this invention, Since the vaporized gas feed pipe 14 which connects the reaction chamber 5 with the vaporizer 3 is equipped with the conductance valve 30, The effective area product of the vaporized gas feed pipe 14 can be changed, conductance can be changed, the flow of the gas containing the vaporizing raw material conveyed to the reaction

chamber 5 from the vaporizer 3 can be adjusted, the internal pressure of the vaporizer 3 and the reaction chamber 5 can be respectively kept independent, and supply of the stable vaporizing raw material can be performed.

[0165]<A9. working example 9> <equipment configuration of working example 9> drawing 10 is a schematic diagram showing CVD system 900 for liquid materials by working example 9 of this invention. The inside of the vaporizer 3b is filled up with the minute metal ball 35 in drawing 10. The heater 8b for heating is formed in the vaporizer 3b, and piping which extends from the liquid supply means 2 is connected to the spraying nozzle 4b of the vaporizer 3 via the valve 13, The vaporized gas feed pipe 14b which conveys a vaporizing raw material to the position from which the perpendicular direction differs is connected to the field which counters the field in which the spraying nozzle 4b was formed in the spraying nozzle 4b.

[0166]The introduction valve 37 and the discharge valve 36 for introduction of the minute metal ball 35 and discharge are provided in [of the vaporizer 3b / perpendicular above (it is an opposite direction to gravity) and perpendicular down (it is a forward direction to gravity)]. These valves need to be the structure where a large effective area product is given and the switching action of a valve is hard to be checked with the minute metal ball 35, and, for that purpose, their ball valve is desirable. A ball valve is a valve which bars the flow of a gas or a fluid because a metal sphere takes up a conduction passage, a breakthrough can be provided in a metal sphere, a metal sphere can be rotated, and it can be made to flow through a gas or a fluid by making it a breakthrough and a conduction passage become the same axle. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.

[0167]<Operation of the CVD system of working example 9>, next operation are explained. The vaporizer 3b and the internal minute metal ball 35 are beforehand heated to the prescribed temperature of about 250 ** with the heater 8b, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. The valves 10, 11, 12, and 13 are closed in this state.

[0168]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [Sr(DPM) $_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. It is roughly microatomized by the high-speed dilution gas style which flows into the circumference at the tip of the spraying nozzle 4b, and the liquid material which reached the vaporizer 3 is contacted and evaporated on the surface of the minute metal ball 35 by it.

[0169]Since it dissolves in THF liquid, and residue is produced in part, without the ability to carry out full evaporation depending on the kind and manufacturing method of a raw material even if it solution-izes, if membrane formation is continued for a while, residue accumulates the DPM compound of beta-diketone system, and it will change the evaporation characteristic or will cause particle. For this reason, after discharging the minute metal ball 35 to which the discharge valve 36 was periodically opened in and the residue thing adhered and then shutting the discharge valve 36, the introduction valve 37 is opened and it is filled up with a new minute metal ball in the vaporizer 3b. Thus, the evaporation residue in the vaporizer 3b can always be kept a fixed quantity to below.

[0170]Thus, the liquid material evaporated with the vaporizer 3b, Like conventional

CVD system 2000 for liquid materials which it was conveyed to the reaction chamber 5 side through the vaporized gas feed pipe 14 according to the pressure differential, and was shown in drawing 27, TTIP material gas and oxidizing gas (O_2 etc.) are mixed, and the strontium titanate thin film by a CVD reaction is formed in the film formation substrate 7 surface heated by the heating stage 6.

[0171]As beyond the <a characteristic operation and effect of working example 9> explained, it fills up with the minute metal ball 35 in the vaporizer 3b, and CVD system 900 for liquid materials concerning working example 9 of this invention contacts and evaporates the microatomized liquid material on the surface of the minute metal ball 35. When it becomes residue and adheres to the minute metal ball 35, without the microatomized liquid material evaporating, by operating the discharge valve 36 and the introduction valve 37, and replacing the minute metal ball 35, the evaporation residue in the vaporizer 3b can always be kept a fixed quantity to below, and a vaporizing raw material can be supplied stably.

[0172]The minute metal ball 35 to which residue adhered can be repeatedly used by washing using acid etc. Adhesion residue is efficiently removable, if physical vibration is given in the case of washing and it is made for a metal sphere to rub mutually.

[0173]<A10. working example 10> <equipment configuration of working example 10> drawing 11 is a schematic diagram showing CVD system 1000 for liquid materials by working example 10 of this invention. The buck which the gas diffusion board 15a is formed in drawing 11 so that the end connection of the vaporized gas feed pipe 14 and the introducing pipe 51 may be surrounded inside reaction chamber 5a, and supports the gas diffusion board 15a, It is connected so that it can desorb to the internal surface in which the end connection of the vaporized gas feed pipe 14 and the introducing pipe 51 was provided. The cooler style 38 is formed near the portion to which the buck of the gas diffusion board 15a of the reaction chamber 5a is connected.

[0174]The gas diffusion board 15a is formed using construction material with good thermal conductivity, and the thickness is formed more thickly than the gas diffusion board 15 of the conventional CVD system for liquid materials shown in drawing 27. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.

[0175]<Operation of the CVD system of working example 10>, next operation are explained. The vaporizer 3 is beforehand heated to the prescribed temperature of about 250 ** with the heater 8, a constant rate of dilution gas (N_2) is supplied with the massflow controller 9, and dilution gas is spouted from the circumference of the spraying nozzle 4. The valves 10, 11, 12, and 13 are closed in this state.

[0176]If the valves 11, 12, and 13 are opened in membrane formation, with the valve 10 closed, a constant rate of liquid materials [Sr(DPM) $_2$+THF] will be sent out towards the vaporizer 3 from the liquid supply means 2. At the tip of the spraying nozzle 4, it is roughly microatomized by the high-speed dilution gas style which flows into the circumference, and the liquid material which reached the vaporizer 3 is evaporated by it. The evaporated liquid material is conveyed to the reaction chamber 5a side by the pressure differential through the vaporized gas feed pipe 14, and the TTIP material gas and oxidizing gas (O_2 etc.) which were evaporated with the bubbling apparatus which is not illustrated are given via the introducing pipe 51, and it is mixed with the vaporized liquid material. The uniform rate of flow distributes with the gas diffusion board 15a, and

mixed gas is diffused in the reaction chamber 5a maintained at the constant pressure.
[0177]The diffused mixed gas contacts the film formation substrate 7 surface heated by the heating stage 6, and forms the strontium titanate thin film by a CVD reaction. The mixed gas which did not contribute to thin film forming is discharged outside via the vacuum pump 17 from the exhaust line 16.
[0178]Although the surface of film formation substrate temperature is 500-700 ** at this time, By forming the cooler style 38 in the wall of the reaction chamber 5a, and connecting the buck of the gas diffusion board 15a to it near the cooler style 38, the heat which the gas diffusion board 15a received from the heating stage 6 can be efficiently told to the cooler style 38, and the rise in heat of the gas diffusion board 15a can be controlled. For this reason, it is prevented that a trap is carried out also in reactant good mixed gas by 15 h of diffusion mouths of the gas diffusion board 15a, it is stabilized, and a strontium titanate thin film can be formed.
[0179]Since desorption of the gas diffusion board 15a is possible, removal of the resultant adhering to the gas diffusion board 15a can be performed easily.
[0180]As beyond the <a characteristic operation and effect of working example 10> explained, CVD system 1000 for liquid materials concerning working example 10 of this invention, Since the gas diffusion board 15a can be cooled and the rise in heat by the heat from the heating stage 6 can be controlled, mixed gas is efficiently supplied to a wafer and stable membrane formation can be realized.
[0181]<A11. working example 11> <equipment configuration of working example 11> drawing 12 is a schematic diagram showing CVD system 1100 for liquid materials by working example 11 of this invention. In drawing 12, the field where the diffusion mouth of the gas diffusion board 15 was provided in the reaction chamber 5 is countered, the heating stage 6a is formed, and account installation of the film formation substrates 7, such as silicon, is carried out on this heating stage 6a. Unlike the conventional heating stage 6 shown in drawing 27, the heating stage 6a has a thermal protection structure. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0182]The expanded sectional view of the heating stage 6a is shown in drawing 13. In drawing 13, the film formation substrate 7 is held, the wafer susceptor 42 which has a function as a heating element, and the wafer susceptor 42 are contacted, and the heater 41 which heats the wafer susceptor 42 is formed. The wafer susceptor 42 and the heater 41 are surrounded by the heat-insulating element 45 except the buildup area of the film formation substrate 7 of the wafer susceptor 42.
[0183]The heat-insulating element 45 may be formed with a metal plate which serves as the structure where an inside is vacuum space so that it may form with SiO2 [high] or Ceramics Sub-Division of adiabatic efficiency or the wafer susceptor 42 and the heater 41 may be surrounded.
[0184]The wafer susceptor 42 and the heater 41 which were enclosed by the heat-insulating element 45 are accommodated in the heater cover 43 formed with the construction material excellent in thermal conductivity, such as aluminum. In order to control the rise in heat by the heat transmitted from the heater 41 to the heater cover 43, the passage 44 for cooling fluid which circulates through cooling fluid is established in the inside of the wall surface of the heater cover 43.
[0185]In drawing 13, although the passage 44 for cooling fluid showed the example

provided in the inside of the wall surface of the heater cover 43, it may join a metal tube to the wall surface outside of the heater cover 43, and may form the passage 44 for cooling fluid.
[0186]<Operation of the CVD system of working example 11>, next operation are explained. 500-700 ** of temperature of the heater 41 is set up at the time of membrane formation. As for heat conduction from the heater 41 to the heater cover 43, most is barred by the heat-insulating element 45 at this time. The heater cover 43 is excellent in thermal conductivity, and since cooling fluid is flowing into the passage 44 for cooling fluid, the rise in heat by the heat transmitted from the heater 41 via the heat-insulating element 45 is controlled, and it can maintain the temperature of the heater cover 43 in the range of 200-250 **. For this reason, in the surface of the heater cover 43 exposed to the reaction chamber 5. $Sr(DPM)_2$ which is a raw material also being condensed, and a BST film are formed -- things -- since there is nothing, such output deposited by prolonged continuous running exfoliates gradually, and the problem that particle occurs in the reaction chamber 5 is solved.
[0187]As beyond the <a characteristic operation and effect of working example 11> explained, CVD system 1100 for liquid materials concerning working example 11 of this invention, In the heating stage 6a in the reaction chamber 5, by insulating the heat given to the heater cover 43 from the heater 41, and cooling the heater cover 43, the rise in heat by the heat transmitted from the heater 41 is controlled, and the temperature of the heater cover 43 can be maintained in the range of 200-250 **. Therefore, even if the output of $Sr(DPM)_2$, a BST film, etc. is not formed in the surface of the heater cover 43 exposed to the reaction chamber 5 but it performs prolonged continuous running, generating of the particle resulting from such output is controlled, and stable membrane formation can be realized.
[0188]<Equipment configuration of A12. working example 12> drawing 14 is a schematic diagram showing the exhaust system containing the reaction chamber 5 and the vacuum pump 17 of CVD system 1200 for liquid materials by working example 12 of this invention. In drawing 14, the cold trap 48 provided with the heat exchanger 47 for cooling between the valve 65 and the vacuum pump 17 is formed in the exhaust system connected to the reaction chamber 5.
[0189]The cold trap 48 is constituted so that exhaust air by the vacuum pump 17 may not be barred, and the internal surface is always maintained at the room temperature grade by the heat exchanger 47 for cooling. It is connected to the valve 65 and the vacuum pump 17 by the terminal areas 60 and 61, and the cold trap 48 can be desorbed from an exhaust line.
[0190]<Operation of the CVD system of working example 12>, next operation are explained. The steams 52, such as a gas material contributed to neither the resultants 51, such as BST formed in the reaction chamber 5, nor membrane formation, flow into an exhaust system. Here, the inner surface of the reaction chamber 5, the exhaust line, and the valve 65 is maintained by 200-250 ** with the heat from the heater 6, and condensation of the resultant 51 and the gas material 52 does not break out. Since the inner surface of the cold trap 48 is cooled by the room temperature grade by the heat exchanger 47 for cooling to this, when the resultant 51 and the gas material 52 pass through the inside of the cold trap 48, it contacts and condenses inside, and the condensation object 53 is formed. For this reason, since the resultant 51 and the gas

material 52 do not amount to 17 in a vacuum pump, the fall of the exhausting capability of the vacuum pump 17 etc. is controlled, and reduction of available time can be prevented.
[0191]When the condensation object 53 is accumulated, the valve 65 is closed, and the cold trap 48 can be removed in the terminal areas 60 and 61, and it can exchange or wash.
[0192]As beyond the <a characteristic operation and effect of working example 12> explained, CVD system 1200 for liquid materials concerning working example 12 of this invention, In the exhaust system connected to the reaction chamber 5, by forming the cold trap 48, It can prevent the resultant 51 and the gas material 52 flowing into vacuum pump 17 grade from a reaction chamber, the fall of the exhausting capability of the vacuum pump 17 etc. is controlled, and reduction of available time can be prevented.
[0193]Although the reaction chamber 5 and the vaporizer 3 explained the device formed independently with the CVD system for liquid materials of working example 1 - working example 12 shown in <A13. working example 13> <equipment configuration of working example 13> drawing 1 - drawing 14, This example explains the CVD system for liquid materials with which the reaction chamber and the vaporizer were united.
[0194]Drawing 15 is a schematic diagram showing CVD system 1300 for liquid materials by working example 13 of this invention. In drawing 15, it is [the vaporizer 103] united and it is formed in the reaction chamber 105 at the lower part (drawing 15 is met and it is the bottom) of the reaction chamber 105.
[0195]It is sealed by the vaporizer 103 and the liquid material container 101 with which the liquid material (here [Sr(DPM) $_2$+THF]) was stored is connected to it. The connecting relation is explained below.
[0196]The valve 110 is formed so that piping which extends from the one end of the valves 111 and 112 may be connected to the liquid material container 101 and between the another side ends of the valves 111 and 112 may be connected. The liquid supply means 102 of a fluid massflow controller, a metering pump, etc. is connected to the another side end of the valve 111, and piping which extends from the liquid supply means 102 is connected to the spraying nozzle 104 of the vaporizer 103 via the valve 113. The another side end of the valve 112 is connected to the nitrogen (N_2) gas supply source which is not illustrated. Although [Ba(DPM) $_2$+THF] etc. are stored in the liquid material container 101a, since the circumference composition is the same as that of the liquid material container 101, explanation is omitted.
[0197]Multipoint connection of the dilution gas feed pipe 192 is carried out to the downstream of the valve 13 of piping which extends from the liquid supply means 102 and is connected to the spraying nozzle 104 of the vaporizer 103 via the valve 113 via the valve 122. The end of the dilution gas feed pipe 191 is connected to the N_2 gas supply source which is not illustrated via the massflow controller 124. The spraying nozzle 104 is arranged at the same axle in the dilution gas feed pipe 191 which has a bigger diameter than this nozzle 104, the end of the dilution gas feed pipe 191 is connected to the massflow controller 109, and the massflow controller 109 is connected to the N_2 gas supply source which is not illustrated. The TTIP raw material vaporized with the bubbling apparatus which is not illustrated and the introducing pipe 151 which supplies oxidizing gas (O_2 etc.) are connected to the vaporizer 103. The vaporizer heating heater 108 is formed in the vaporizer 103. On the other hand, the cooler style 138 is formed in the inside of the wall surface of the vaporizer 103 and the vaporizer 103 near the terminal

area of the reaction chamber 105. This is for keeping constant the temperature of the 1st and 2nd current plates 154 and 155 explained later and the gas diffusion board 115.

[0198]The 1st current plate 154 and the 2nd current plate 155 are formed in the opening of the vaporizer 103 facing reaction chamber 105 inside sequentially from the vaporizer 103 side. Although the 1st current plate 154 and the 2nd current plate 155 are formed in order for the raw material which became residue without being evaporated with the vaporizer 103 to prevent trespassing upon the reaction chamber 105, and the 1st current plate 154 has **** in the center section, It has prevented trespassing upon the reaction chamber 105 in the state where a circle gossip part is bent toward vaporizer 103 inside, makes small the solid angle from the spraying nozzle 104, and blows off from the spraying nozzle 104, and the microatomized liquid material does not evaporate.

[0199]The sectional shape of the 2nd current plate 155 is the type of KO, and it is established so that it may project a little toward reaction chamber 105 inside from the opening of the vaporizer 103 and an opening may be covered. Two or more penetrating ports are formed in the upper surface and the side of the 2nd current plate 155, and the vaporizing raw material evaporated with the vaporizer 103 can be supplied in the reaction chamber 105.

[0200]The gas diffusion board 115 is formed in reaction chamber 105 inside so that the 2nd current plate 155 may be covered. In a field parallel to the film formation substrate 107 of the gas diffusion board 115. The gas stream of a vaporizing raw material is distributed uniformly, and two or more diffusion mouths 156 and 157 for supplying the film formation substrate 107 surface are formed respectively, among these the diffusion mouth 157 is connected with the charging line 158 of reactant high oxidizing gas, such as ozone (O_3) and N_2O. The gas diffusion board 115 comprises metal excellent in thermal conductivity, such as aluminum, in order to make temperature distribution uniform.

[0201]The film formation substrate 107 is held at the wafer susceptor 142 made from silica glass. The wafer susceptor 142 maintains space at the support plate 190 formed above that in the reaction chamber 105, and is being fixed to it. Between the support plate 190 and the wafer susceptor 142, two or more light reflectors 160 are formed in order from the support plate 190, and the infrared lamp heater 159 is formed corresponding to each light reflector 160. The support plate 190 has structure which does not bar exhaust air by the exhaust system connected to the reaction chamber 105. The exhaust system equips the exhaust line 116 with the gate valve 146 and the vacuum pump 117.

[0202]The reaction chamber heating heater 161 is formed in the surface of the reaction chamber 105, and regulation of the temperature of the wall surface of the reaction chamber 105 is possible.

[0203]<Operation of the CVD system of working example 13>, next operation are explained. First, the substrate 107 is fixed to the wafer susceptor 142 made from silica glass. Then, it energizes to the infrared lamp heater 159, the reaction chamber heating heater 161, and the vaporizer heating heater 108, After heating the vaporizer 103, and the internal surface and the gas diffusion board 115 of the reaction chamber 105 to a predetermined temperature, Reactant gas (here oxidizers, such as oxygen) is supplied from the piping 151, a constant rate of gas for dilution (here N_2) is supplied with the massflow controller 109 and the massflow controller 124, and dilution gas is spouted from the spraying nozzle 104 and its circumference. The valves 110, 111, 112, and 113 are closed in this state.

[0204]If the valves 111, 112, and 113 are opened with the valve 110 closed after heating the film formation substrate 107 to forming temperature with the infrared lamp heater 159, a constant rate of liquid materials [Sr(DPM) $_2$+THF] will be sent out towards the vaporizer 103 from the liquid supply means 102. It is roughly microatomized by the high-speed dilution gas style which flows into the circumference at the tip of the spraying nozzle 104, and the liquid material which reached the vaporizer 103 carries out a distributed collision at the wide range of the wall of the vaporizer 103, is evaporated in an instant, and is mixed with the oxidizer and TTIP which were supplied from the piping 151. With the 1st and 2nd current plate 154 and 155, it is mixed further, it is equalized and mixed gas is emitted. the emitted mixed gas passes the diffusion holes 156 of the gas diffusion board 115 -- etc. -- it is supplied toward the film formation substrate 107 at the rate of flow. The supplied mixed gas is decomposed the surface top of the film formation substrate 107, or near the surface, the thin film of uniform thickness is formed on the film formation substrate 107, and residual cracked gas and resultant are exhausted out of a reaction chamber through the exhaust line 116.
[0205]In the process of membrane formation, oxidation of the STO membrane surface deposited on the film formation substrate 107 is promoted by supplying intermittently reactant high oxidizing gas, such as ozone (O_3) and N_2O, from the diffusion mouth 157 of the gas diffusion board 115.
[0206]The annealing effect which promotes crystallization of ST film can be acquired by increasing the output of the infrared lamp heater 159 periodically, and heating the temperature of the film formation substrate 107 to about 700 ** during membrane formation.
[0207]By what the cooler style 138 is formed in the inside of the wall surface of the vaporizer 103 and the vaporizer 103 near the terminal area of the reaction chamber 105 for. Since the temperature of the 1st and 2nd current plates 154 and 155 and the gas diffusion board 115 is kept constant, supply of mixed gas can be prevented from a resultant being formed in the penetrating port of the 2nd current plate 155, or the diffusion mouth of the gas diffusion board 115, and being checked.
[0208]As beyond the <a characteristic operation and effect of working example 13> explained, CVD system 1300 concerning working example 13 of this invention, Since it is [the vaporizer 103] united and it is formed in the reaction chamber 105, piping for vaporizing raw material transportation which connects the reaction chamber 105 with the vaporizer 103 becomes unnecessary, and becomes unnecessary [the mechanism which maintains this piping at an elevated temperature in connection with it].
[0209]When oxidizing gas, such as ozone, performs oxidation treatment for oxide stock high permittivity thin films, such as strontium titanate and barium titanate, Since mixing of oxidizing gas and material gas is not performed by the inside of the gas diffusion board 115, but oxidizing gas is supplied from the charging line 158 connected with the diffusion mouth 157 of the gas diffusion board 115 and mixing of oxidizing gas and material gas is performed on the film formation substrate 107, the raising dust accompanying mixing of oxidizing gas and material gas is controlled.
[0210]When performing annealing treatment to oxide stock high permittivity thin films, such as strontium titanate and barium titanate, and raising crystallinity, Since the output of the infrared lamp heater 159 is increased periodically and the temperature of the film formation substrate 107 can be raised during membrane formation, The process which

takes out the film formation substrate 107 and is changed to a high-temperature-processing chamber becomes unnecessary, and the problem that the film formation substrate 107 is put to the atmosphere, combines with CO_2, and forms barium carbonate is solved.
[0211]<A14. working example 14> <equipment configuration of working example 14> drawing 16 is a sectional view showing the liquid material container 1c of CVD system 1400 for liquid materials by working example 14 of this invention, and the composition of the circumference of it. Since the composition of others of CVD system 1400 for liquid materials is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the figure of a portion is omitted similarly.
[0212]In drawing 16, the liquid material container 1c with which the liquid material 84 was stored comprises the package body 87 which accommodates the liquid material 84, and the container lid 86 which seals the package body 87, and the sealant 82 for sealing is formed between the package body 87 and the container lid 86. The package body 87 and the container lid 86 are fixed by the fixing means of the fixing screw 83 etc. so that the sealant 82 may be pressed.
[0213]Connected to the container lid 86 so that the piping P11 and P12 which extends from the one end of the valves 11c and 12c might penetrate the container lid 86, at least one side of the piping P11 and P12 has reached in the liquid material 84. The joints 39c and 40c are formed in each another side end of the valves 11c and 12c. In the package body 87, it has the dehydrator 85 for adsorbing the moisture mixed in the liquid material 84. Here, the trap pack G084033 (Limited, Nihon Millipore) containing a molecular sieve, etc. are used for the dehydrator 85, for example.
[0214]The liquid material containers 1 and 1a which showed working example 1 - working example 13 of the CVD system for liquid materials explained using drawing 1 - drawing 15 the composition of the liquid material container 1c explained above, The reference mark of the valves 11c and 12c and the joints 39c and 40c has only changed that it is composition common to 1b, 101, and 101a. Since other composition is the same as that of conventional CVD system 2000 for liquid materials shown in drawing 27, the overlapping explanation is omitted.
[0215]As operation of the CVD system of <operation of CVD system of working example 14> working example 14, the directions of the liquid material container 1c are explained. Raw material filling work is performed in the vacuum glove box which performed inert gas replacement by high grade N_2 with a moisture concentration of 0.5 PPM or less. Stoving of the container part article is beforehand carried out by a vacua. After cooling, after filling up the package body 87 with the liquid material 84 and the dehydrator 85 which were dried in moisture concentration of 10 PPM or less, the container lid 86 is fixed to the package body 87 via the sealant 82 using the fixing screw 83. The joints 39c and 40c could put the cap, and have also closed the valves 11c and 12c, and airtightness is maintained. The ingredient container 1c is connected to a CVD system via the joints 39c and 40c.
[0216]Into the ingredient container 1c prepared in this way, moisture invades gradually by the feeding gas for supplying the liquid material 84 to a CVD system, and leak of the ingredient container 1c. The dehydrator 85 adsorbs such moisture and degradation by moisture mixing in DPM compounds, such as Ba and Sr, is controlled.
[0217]<a characteristic operation and effect of working example 14> -- using this

ingredient container 1c, When the evaporation experiment of the THF solution (0.1 mol/l) of Ba(DPM) $_2$ was conducted 30 times over one month, generating in particular of the residue of Ba(DPM) $_2$ by the order of an evaporation un-of the THF solution of Ba(DPM) $_2$ was not seen, but showed the good evaporation characteristic.

[0218]Working example of the CVD process using the liquid material by <working example of the CVD process using B. liquid material>, next this invention is described using drawing 17 - drawing 26. First, the liquid material which dissolved Ba(DPM) $_2$ of the liquid material and solid which dissolved solid Sr(DPM) $_2$ in THF in THF, Mix Ti vaporizing raw material which made TTIP [Ti(O-i-$C_{3\ H7)\ 4}$] which is a raw material of Ti evaporate by bubbling, and it is considered as material gas, Add O_2, it is made to react furthermore and the example which forms a barium strontium titanate (Ba, Sr) TiO_3 film (it is henceforth written as a BST film) on a substrate is shown.

[0219]The example which raises the crystallinity of the formation initial part of the BST film which performs gradual membrane formation and is easy to make it amorphous, and raises the electrical property of the whole BST film is shown.

[0220]By using the same DPM system raw material as Ba and Sr as low-temperature-izing and Ti raw material of film formation substrate temperature shows the example which aimed at improvement in step coverage nature.

[0221]Although CVD systems 100-1400 for liquid materials of this invention explained in working example 1 - working example 14 can also be used as a CVD system for liquid materials for carrying out the CVD process of this invention, In order to simplify explanation, conventional CVD system 3000 for liquid materials shown in drawing 28 is used. In the CVD process of this invention, since N_2O is added as an oxidizer in addition to O_2 at the time of membrane formation, the mechanism which supplies N_2O in addition to O_2 is added to CVD system 3000 for liquid materials shown in drawing 28.

[0222]<B1. working example 15> drawing 17 is a sectional view of the BST film formed of the CVD process of working example 15 of this invention. In drawing 17, BST film L4 formed by adding N_2O is formed on the lower Pt electrode L3 of the substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on the same Si substrate L1 as usual.

[0223]Before forming BST film L4 on the lower Pt electrode L3, in order to prevent the partial electric short circuit which removes the foreign matter of the surface of the lower Pt electrode L3, and is produced for a foreign matter, Mechanical polish (Chemical Mechanical Polishing) is given to the surface of the lower Pt electrode L3, or HF (fluoric acid) washing is performed instead of mechanical polish.

[0224]The addition of O_2 in the CVD process of the <example of the experiment of CVD process of working example 15> former by flow conversion (it is henceforth called an O_2 flow) In the case of 6slm. As working example of the CVD process of this invention, about two conditions in case the addition of N_2O is 2slm in flow conversion (it is henceforth called an N_2O flow) in addition to O_2 flow 4slm. The preset temperature of internal pressure 10Torr of the reaction chamber 5 and a heating stage shall be 650 **, Control a liquid material flow and membrane formation time, and Composition ratio (Ba+Sr)/Ti=1.0 of a BST film, 1000 A of thickness, The leakage current density at the time of the oxide film conversion thickness of the BST film obtained by performing membrane formation for 20 minutes by 50 A in membrane formation speed / min and direct-current-voltage 1.65V impression was measured, respectively. It is shown in Table

1 by making the result into the example 1 of an experiment.
[0225]
[Table 1]

実験例番号	酸化剤流量 (slm)	誘電容量 (nF)	誘電正接	換算膜厚 (nm)	比誘電率	リーク電流密度 (A/cm^2)
1	O_2：6	110	0.04	0.35	887	1×10^{-6}
	O_2：4，N_2：2	112	0.02	0.34	827	2×10^{-6}

[0226]Measurement measures in a similar manner by nine points in a field, and shows the average value in Table 1. As opposed to being dielectric dissipation factor 0.04, 0.35 nm of oxide film conversion thickness, and leakage current density $1x10^{-6}A/cm_2$, when an O_2 flow is 6slm in the conventional CVD process, When N_2O was added, it was dielectric dissipation factor 0.02, 0.34 nm of oxide film conversion thickness, and leakage current density $2x10^{-6}A/cm_2$.
[0227]The example of < experiment shows that the directions which added N_2O decrease in number in a dielectric dissipation factor, oxide film conversion thickness, etc., and the electrical property is improving so that clearly from the consideration > table 1. The place which investigated the structure of the BST film which does not add N_2O, and the BST film which added N_2O according to the X diffraction, It turned out that the peak waveform which both shows existence of the field (100) of a BST crystal, a field (110), and a field (111) is observed, and the BST film which has a perovskite structure is formed.
[0228]The peak waveform of the field (111) of $BaCO_3$ slightly contained as an impurity was understood that the direction of the BST film which added N_2O has small peak intensity. It turned out that it is effective in removing an impurity from this by adding N_2O.
[0229]From the result of the example 1 of an experiment explained above, the CVD process of this invention which adds N_2O proved that the electrical property and membraneous quality of a BST film can be improved.
[0230]<B-2. working example 16> drawing 18 is a sectional view of the BST film formed of the CVD process of working example 16 of this invention. The substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on Si substrate L1 in drawing 18, On the lower Pt electrode L3, the initial film L5 of BST which performed lamp annealing processing is formed, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.
[0231]<the example of an experiment of the CVD process of working example 16> -- the example of single step membrane formation is first explained as usual membrane formation. As an oxidizer an O_2 flow by carrying out 2slm supply of 4slm and the N_2O flow, and making it react to a vaporizing raw material by the preset temperature of internal pressure 10Torr of the reaction chamber 5 and a heating stage being 550 **, On lower Pt electrode layer L3 of a substrate, a liquid material flow and membrane formation time were controlled, membrane formation for 20 minutes was performed by composition

ratio (Ba+Sr)/Ti=1.0 of a BST film, 1000 A of thickness, and 50 A in membrane formation speed / min, and the BST film was formed.
[0232]Next, the example of gradual membrane formation is shown. The inside of the reaction chamber 5 is under the O_2 atmosphere of pressure 10Torr, and since coverage is as good as low temperature, the preset temperature of the heating stage 6 shall be 550 **, A liquid material flow and membrane formation time are controlled on the lower Pt electrode L3 of the foundation layer which is made to react to TTIP, O_2, and material gas and by which the SiO_2 layer and lower Pt electrode layer L3 were formed in order on Si substrate L1, Membrane formation for 2 minutes is performed by composition ratio (Ba+Sr)/Ti=1.0 of a BST film, 1000 A of thickness, and 50 A in membrane formation speed / min, and the initial film L5 of BST is formed.
[0233]Then, it takes out from the reaction chamber 5 and lamp annealing is performed. A sample is again returned to the reaction chamber 5 after annealing, under the pressure of 10Torr, the preset temperature of the heating stage 6 shall be 550 **, and latter-part BST film L6 is formed by membrane formation for 18 minutes. It is shown in Table 2 by making into the example 2 of an experiment the result of the usual membrane formation explained above and stage membrane formation.
[0234]
[Table 2]

実験例番号		誘電容量 (nF)	誘電正接	換算膜厚 (nm)	比誘電率	リーク電流密度 (A/cm^2)
2	一段階成膜	12	0.02	3.22	83	5×10^{-8}
	二段階成膜	77	0.06	0.49	859	3×10^{-5}

[0235]As opposed to being dielectric dissipation factor 0.02, 3.22 nm of oxide film conversion thickness, and leakage current density $5x10^{-8}A/cm^2$ in single step membrane formation so that clearly from Table 2, In gradual membrane formation, it was dielectric dissipation factor 0.06, 0.49 nm of oxide film conversion thickness, and leakage current density $3x10^{-5}A/cm^2$.
[0236]It turns out that lamp annealing processing is performed after formation of the initial film L5 of consideration >BST as a result of the example of < experiment, oxide film conversion thickness decreases substantially and the electrical property is improving by gradual membrane formation which forms latter-part BST film L6 on it. By performing lamp annealing processing after formation of the initial film L5 of BST, the initial film L5 of BST is crystallized and this shows that the electrical property of the whole BST film has been improved.
[0237]<B3. working example 17> drawing 19 is a sectional view of the BST film formed of the CVD process of working example 17 of this invention. In drawing 19, the initial film L7 of BST which performed O_3 processing is formed on the lower Pt electrode L3 of the substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on Si substrate L1, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.

[0238]Although working example 16 of this invention showed the initial film L5 of BST which performed lamp annealing processing in gradual membrane formation, Also by performing O_3 processing which puts the initial film L7 of BST immediately after formation to O_3 atmosphere instead of lamp annealing processing, crystallization of the initial film L7 of BST can be attained, and the electrical property of the whole BST film can be improved.
[0239]<B4. working example 18> drawing 20 is a sectional view of the BST film formed of the CVD process of working example 18 of this invention. In drawing 20, on the lower Pt electrode L3 of the substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on Si substrate L1, The initial film L9 of BST which performed O_2 plasma treatment is formed, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.
[0240]Although working example 16 of this invention showed the initial film L5 of BST which performed lamp annealing processing in gradual membrane formation, Also by performing O_2 plasma treatment which puts the initial film L9 of BST immediately after formation to O_2 plasma instead of lamp annealing processing, crystallization of the initial film L9 of BST can be attained, and the electrical property of the whole BST film can be improved.
[0241]<B5. working example 19> drawing 21 is a sectional view of the BST film formed of the CVD process of working example 21 of this invention. In drawing 21, on the lower Pt electrode L3 of the substrate with which the SiO_2 layer and lower Pt electrode layer L3 were formed in order on Si substrate L1, The initial film L10 of BST which was made to increase an O_2 flow and was formed is formed, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.
[0242]Although working example 16 of the CVD process of this invention showed the example which formed the initial film L5 of BST with the manufacturing method of the conventional BST film using $O_2$4slm and N_2O2slm as an oxidizer in gradual membrane formation, make an O_2 flow increase, and an O_2 flow 6slm, Also by carrying out 2slm supply of the N_2O flow, and forming the initial film L10 of BST, the crystallized initial film L10 of BST is obtained, and the electrical property of the whole BST film can be improved.
[0243]<B6. working example 20> drawing 22 is a sectional view of the BST film formed of the CVD process of working example 20 of this invention. In drawing 22, the initial film L11 of BST which changed and formed composition ratio on the lower Pt electrode L3 of the substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on Si substrate L1 is formed, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.
[0244]In working example 16 of this invention, in gradual membrane formation, it is formed so that the presentation of the initial film L5 of BST may be set to (Ba+Sr)/Ti=1, but it may form so that composition ratio may be set to (Ba+Sr)/Ti=1.1.
[0245]At 530 **, the crystallinity of a BST film is large to membranous composition ratio (Ba+Sr)/Ti, and the preset temperature of a heating stage depends for this, Since it turns out experimentally that an amorphous-like film is obtained by the film crystallized or more by one bordering on the composition ratio 1, and 1 or less, the amount of material flow is adjusted so that it may become the presentation which the initial film of BST tends to crystallize, and the initial film L11 of BST is formed. Latter-part BST film

L6 makes preset temperature of the heating stage 6 550 **, and it adjusts and forms the amount of material flow so that a presentation may be set to (Ba+Sr)/Ti=1. Also by this method, the crystallized initial film L11 of BST is obtained, and the electrical property of the whole BST film can be improved.
[0246]<B7. working example 21> drawing 23 is a sectional view of the BST film formed of the CVD process of working example 21 of this invention. In drawing 23, on the lower Pt electrode L3 of the substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on Si substrate L1, The initial film L12 of BST which changed and formed membrane formation speed is formed, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.
[0247]Although working example 16 of this invention showed the example which controlled a liquid material flow and membrane formation time, performed membrane formation for 2 minutes by 50 A in membrane formation speed / min, and formed the initial film L5 of BST on the lower Pt electrode L3 in gradual membrane formation, Also by decreasing the amount of feeding and reducing membrane formation speed, the initial film L12 of BST is crystallized and the electrical property of the whole BST film can be improved.
[0248]Membrane formation speed may be reduced by increasing the amount of supply of an oxidizer and making a reaction chamber pressure increase. Also by this method, the crystallized initial film L12 of BST is obtained, and the electrical property of the whole BST film can be improved.
[0249]<B8. working example 22> drawing 24 is a sectional view of the BST film formed of the CVD process of working example 22 of this invention. In drawing 24, on the lower Pt electrode L3 of the substrate with which the SiO_2 layer L2 and lower Pt electrode layer L3 were formed in order on Si substrate L1, The $SrTiO_3$ film (it is henceforth written as ST film) L13 is formed, and latter-part BST film L6 which formed membranes on condition of the former as gradual membrane formation is formed on it.
[0250]The preset temperature of the <example of the experiment of CVD process of working example 22> heating stage 6 shall be 550 **, Sr vaporizing raw material which made the liquid material which dissolved $Sr(DPM)_2$ in the organic solvent THF like the time of the conventional BST film formation heat and evaporate in the vaporizer 3, Mix Ti vaporizing raw material which made TTIP which is a raw material of Ti evaporate by bubbling, and it is considered as material gas, On the lower Pt electrode L3 of the substrate with which material gas and an oxidizer (O_2) were made to react, and the SiO_2 layer and lower Pt electrode layer L3 were formed in order on Si substrate L1, membrane formation for 2 minutes is performed and the ST film L13 is formed as an initial film.
[0251]Then, Sr vaporizing raw material, Ba vaporizing raw material, and Ti vaporizing raw material that made TTIP evaporate by bubbling shall be mixed, it shall be considered as material gas, an oxidizer (O_2) shall be added, the preset temperature of the heating stage 6 shall be 550 **, and latter-part BST film L6 is formed by membrane formation for 18 minutes. It is shown in Table 3 by making the measurement result of the electrical property of the obtained BST film into the example 3 of an experiment. The measurement result of the electrical property of the BST film by the single step membrane formation shown in Table 2 of working example 16 is also collectively shown in Table 3.
[0252]

[Table 3]

実験例番号		誘電容量 (nF)	誘電正接	換算膜厚 (nm)	比誘電率	リーク電流密度 (A/cm^2)
3	一段階成膜	12	0.02	3.22	83	5×10^{-8}
	二段階成膜	68	0.08	0.56	531	6×10^{-5}

[0253]When the ST film L13 was formed as an initial film so that clearly from Table 3, it was dielectric dissipation factor 0.08, 0.56 nm of oxide film conversion thickness, and leakage current density $6x10^{-5}A/cm^2$.
[0254]By forming the ST film L13 as consideration >, thus an initial film in gradual membrane formation as a result of the example of < experiment shows that oxide film conversion thickness decreases substantially and the electrical property is improving. By forming the ST film L7 as an initial film in gradual membrane formation, the interface of Pt and the ST film L7 is crystallized, and this shows that the electrical property of the whole BST film has been improved.
[0255]<B9. working example 23> drawing 25 is a sectional view of the BST film formed of the CVD process of working example 23 of this invention. In drawing 25, BST film L17 is formed on the substrate L16 with a level difference which has step shape.
[0256]The <example of an experiment of the CVD process of working example 23> TTIP is supplied by bubbling, the preset temperature of the heating stage 6 is changed on the substrate L16 with a level difference which has step shape, and it is TiO2. The film was formed and the temperature dependence of step coverage nature was investigated. It is shown in Table 4 by making the result into the example 4 of an experiment.
[0257]
[Table 4]

実験例番号	膜種	設定温度 (℃)	dmin／dmax (%)
4	TiO_2	400	40
	TiO_2	550	23
	TiO_2	700	22
	BST	550	38
	BST	500	45

[0258]In Table 4, it turns out that the value of dmin/dmax which shows step coverage nature is improving, so that the preset temperature of the heating stage 6 is low. Then, preset temperature of the heating stage 6 was made lower than before, BST film L17 was formed on the substrate L16 with a level difference which has step shape with the preset temperature of 500 **, and the temperature dependence of step coverage nature was

investigated. The result is combined with Table 4 and shown.
[0259]The value of dmin /dmax which shows the step coverage nature of a BST film was 45% at 500 ** 38% in 550 ** so that clearly from Table 4.
[0260]It turned out by making low consideration >, thus preset temperature of the heating stage 6 as a result of the example of < experiment that step coverage nature becomes good.
[0261]<B10. working example 24> drawing 26 is a sectional view of the BST film formed of the CVD process of working example 24 of this invention. In drawing 25, BST film L19 is formed on the substrate L16 with a level difference which has step shape with the DPM system material of Ba and Sr, and the DPM system material of Ti. Here, TiO(DPM) $_2$ was used as a DPM system material of Ti.
[0262]As shown in Table 4 shown in working example 22 of the CVD process of <example of the experiment of CVD process of working example 24> this invention, in the preset temperature of the same heating stage 6. TiO2 formed with Ti raw material obtained by bubbling of TTIP The step coverage nature of the BST film formed with Ba and Sr raw material of a DPM system is better than a film.
[0263]Then, using the DPM system material of Ba and Sr, and the DPM system material of Ti, BST film L19 was formed and step coverage nature was investigated. It is shown in Table 5 by making the result into the example 5 of an experiment. The BST film was formed on the substrate with a level difference which has step shape using Ti raw material obtained by bubbling of TTIP, and the DPM system material of Ba and Sr, and step coverage nature was investigated. The result is combined with Table 5 and shown.
[0264]
[Table 5]

実験例番号	Ｔｉ原料	設定温度 (℃)	dmin／dmax (%)
5	TTIP	500	45
	TiO(DPM)2	500	80

[0265]The step coverage nature of BST film L19 which formed the value of dmin /dmax which shows the step coverage nature of a BST film to the case where a BST film is formed using TTIP being 45% using TiO(DPM) $_2$ was 80% at 500 ** so that clearly from Table 5.
[0266]It became clear that the BST film using TiO(DPM) $_2$ could form a BST film with good covering nature in this way on the consideration > board L16 with a level difference in which step coverage nature is good and has step shape according to the CVD process of this invention as a result of the example of < experiment. When this raw material is used, Ba, Sr, and all Ti can be supplied by the same system, and simple-izing of a distribution system is also possible.
[0267]As a charge of a DPM system Ti material, Ti(O-iPr) $_2$(DPM) $_2$ is also conjectured that step coverage nature is improved.
[0268]The liquid material used for the CVD system and CVD process of working example 25 of <working example <C1. working example 25> of liquid material> this invention is explained below. In 25 or less working example, it explains using

conventional CVD system 3000 for liquid materials explained by drawing 28.
[0269]The HDPM liquid (independent DPM liquid which has hydrogen) which is a base material of the ligand of $Sr(DPM)_2$ was used as the solvent, it dissolved so that the concentration of $Sr(DPM)_2$ might be 0.2-mol%, and it was considered as the liquid material. The ingredient container 1 was filled up with this and the evaporation experiment was conducted using conventional CVD system 3000 shown in drawing 28. The liquid material which uses THF liquid as a solvent was also prepared for comparison. The evaporation temperature in the vaporizer 3 was 250 **, it evaporated by having repeated 1 time of evaporation time as 30 minutes, and the residue generated in the vaporizer 3 was observed. When THF liquid was used as a solvent, and 17 evaporation experiments were conducted, blackish brown liquefied residue was checked. On the other hand, when HDPM liquid was used as a solvent, even when 30 evaporation experiments were conducted, residue could not be checked, but it became clear that it had the good evaporation characteristic.
[0270]Thus, as a cause by which the evaporation characteristic improved by using HDPM liquid as a solvent, Since a lot of DPM molecules exist in the surroundings of the molecule of $Sr(DPM)_2$, Since degradation of a self-association etc. not taking place easily and Sr(DPM's) $_2$'s being able to exist stably alone and HDPM liquid have steam pressure lower than THF liquid and the steam pressure difference with $Sr(DPM)_2$ is small, it is possible to be uniformly vaporizable.
[0271]The whole quantity of a solvent does not necessarily need to be a base material of a ligand, for example, in the combination of $Sr(DPM)_2$ and HDPM liquid, even when 50% of HDPM liquid is added and used to THF liquid, an equivalent effect is acquired.
[0272]The same effect was acquired also in the combination of $Ba(DPM)_2$ and HDPM. An effect with the same said of other organic metallic compounds, such as Ti, Pb, and Zr, is expectable. The same may be said of the organic metallic compound which has ligands, such as a cyclopentadiene and hexafluoro acetyl chill acetone.
[0273]The liquid material used for the CVD system and CVD process of working example 26 of <C2. working example 26> this invention is explained below. $Ba(DPM)_2$ and $Sr(DPM)_2$ were dissolved by the concentration of 0.1 mol/l into THP liquid, respectively. The ingredient container 1 was filled up with this and the evaporation experiment was conducted at the evaporation temperature of 250 ** using CVD system 3000 shown in drawing 28. To the dilution gas feed pipe 91, the condition of transport from the outside to the vaporizer 3 of a liquid material was observed using the translucent Teflon pipe.
[0274]When the liquid material which uses THF liquid as a solvent was evaporated, it was generated by air bubbles in the dilution gas feed pipe 91 near the vaporizer 3, and the coagulation of moisture expected to be based on evaporation heat occurred around the dilution gas feed pipe 91. When a liquid material was supplied in such a situation, spraying of the liquid material from the tip of the spraying nozzle 4 became intermittent, unevenness was made to the concentration of the gas material by which it is generated within the vaporizer 3, and the phenomenon which is not preferred occurred. When a liquid material with high concentration was used, as explained as a problem of the conventional CVD system, when only THF liquid evaporated, concentration occurred and the organic compound deposited in the dilution gas feed pipe 91.
[0275]On the other hand, when THP was used for a solvent, generating of such air

bubbles and the coagulation of moisture were lost, and the liquid material was uniformly supplied to the vaporizer 3. Especially even if it conducted 30 evaporation experiments or more, generating of the residue in the vaporizer 3 was not accepted.
[0276]The liquid material used for the CVD system and CVD process of working example 27 of <C3. working example 27> this invention is explained below. The evaporation experiment was conducted under the same conditions as working example 26 mentioned above, using 1 and 4-dioxane as a solvent. Generating of residue was not accepted, even if the liquid material was smoothly supplied to the vaporizer 3 and it conducted 30 evaporation experiments or more at the evaporation temperature of 250 ** like the case where THP liquid is used for a solvent.
[0277]The liquid material used for the CVD system and CVD process of working example 28 of <C4. working example 28> this invention is explained below. $Ba(DPM)_2$ and $Sr(DPM)_2$ were dissolved by the concentration of 0.1 mol/l into the carbon tetrachloride which is a nonpolar solvent, or THF liquid, respectively, the ingredient container 1 was filled up with this, and aging of the liquid material was investigated.
[0278]Residual moisture promotes degradation of $Ba(DPM)_2$ and $Sr(DPM)_2$. The trap pack G084033 (Limited, Nihon Millipore) containing a molecular sieve was thrown in, it dried, and any solvent measured moisture concentration with the curl = Fischer water measurement machine. Each moisture concentration was [at THF before drying] below the detection limit in THF after 50 PPM and drying in 10 PPM and a carbon tetrachloride.
[0279]When the evaporation temperature in the vaporizer 3 was 250 **, 1 time of evaporation time was made into 30 minutes, using a carbon tetrachloride as a solvent and 30 evaporation experiments were conducted over one month, residue in particular was not checked. On the other hand, when THF liquid was used as a solvent, and 17 evaporation experiments were conducted, blackish brown liquefied residue was checked. Since THF liquid is a polar solvent, even if it performs water removal, re-moisture absorption once occurs easily in the middle of subsequent filling work or a process.
[0280]The difference of such the evaporation characteristic was checked also by evaporation experiment. That is, generating of residue was not seen, when a solvent was carbon tetrachloride liquid and the evaporation experiment for 30 minutes was conducted 30 times at the evaporation temperature of 250 ** in one month. On the other hand, generating of residue became remarkable when a solvent was THF, and evaporation was performed 7 times.
[0281]Such an effect can be attained also in other nonpolar solvents (for example, benzene, cyclohexane, etc.).
[0282]
[Effect of the Invention]Since the inside of piping can be washed by sending out a solvent to said piping from a solvent container according to the CVD system for liquid materials of this invention according to claim 1, a liquid material can prevent solidifying within piping at the time of liquid material container exchange.
[0283]Since the sending-out speed of the liquid material sent out to a vaporizer from an ingredient container by having had the inactive gas charging line can be raised according to the CVD system for liquid materials of this invention according to claim 2, residue can be prevented from sending out to a vaporizer, without making a liquid material evaporate, and adhering in piping.

[0284]Since the inactive gas which flows through the inside of an inactive gas feed pipe by having had the inactive gas cooling method further can be cooled according to the CVD system for liquid materials of this invention according to claim 3, residue can be prevented from sending out to a vaporizer, without making a liquid material evaporate, and adhering in piping.
[0285]According to the CVD system for liquid materials of this invention according to claim 4, residue can be prevented from preventing evaporation within piping of a liquid material and adhering in piping by sending out solvent liquid to an inactive gas charging line.
[0286]According to the CVD system for liquid materials of this invention according to claim 5, to the receiving container kept the same as that of the internal pressure of a vaporizer. The controllability of the flow of a liquid material can be improved because only fixed time until the flow of a liquid material becomes fixed slushes a liquid material and changes the flow of a liquid material to the vaporizer side after that.
[0287]Since the evaporation characteristic of the liquid material influenced by the pressure in piping since it has the regulating valve which adjusts the pressure in piping according to the CVD system for liquid materials of this invention according to claim 6 is controllable, residue can be prevented from preventing evaporation within piping of a liquid material and adhering in piping.
[0288]According to the CVD system for liquid materials of this invention according to claim 7, by the thing of piping for which the neighborhood of a vaporizer is formed by PTFE at least. Since residue does not adhere to PTFE which has the smooth surface easily also when evaporation of the liquid material by heat conduction is reduced and the residue of a liquid material occurs, residue can be prevented from being accumulated into piping.
[0289]According to the CVD system for liquid materials of this invention according to claim 8, residue can be prevented from reducing the rise in heat of piping, and a liquid material evaporating within piping, and being accumulated by having established the wrap-shaped piping cooling method for piping near the vaporizer of piping.
[0290]Since according to the CVD system for liquid materials of this invention according to claim 9 a liquid material is given to a forward direction to gravity and the vaporized liquid material is sent out to an opposite direction to gravity, The residue of a liquid material can be prevented from being accumulated into a vaporizer, and the liquid material and residue which are not evaporated [floating] can be prevented from being sent out to a reaction chamber.
[0291]When according to the CVD system for liquid materials of this invention according to claim 10 it fills up with the minute metal ball by which the temperature rise was carried out to the inside of a vaporizer and a liquid material contacts and evaporates in a minute metal ball, When evaporation of a liquid material is attained and the residue of a liquid material adheres to a minute metal ball, the inside of a vaporizer can be defecated by exchanging a minute metal ball.
[0292]According to the CVD system for liquid materials of this invention according to claim 11, by having had the valve for opening sectional area adjustment near the vaporizer. Since the degree of opening and closing of a valve can be adjusted, the effective area product of piping can be changed and the pressure in a vaporizer can be kept independent of a reaction chamber, also when changing the pressure in a reaction

chamber, the pressure in a vaporizer can be kept constant.
[0293]Since the temperature of a gas diffusion board can be kept constant by cooling a gas diffusion board by the cooling method provided in the field to which a gas diffusion board contacts according to the CVD system for liquid materials of this invention according to claim 12, gas with low decomposition temperature can be prevented from adhering to a gas diffusion board.
[0294]Since the heating element and the conductor are insulated by the heat-insulating element to the supporter in susceptor according to the CVD system for liquid materials of this invention according to claim 13, a supporter is prevented from being heated and a resultant can be prevented from accumulating on the periphery of a supporter.
[0295]Since a liquid material and a reactant gas can be prevented from reaching an exhaust means since the exhaust means is provided with the gas adsorption means according to the CVD system for liquid materials of this invention according to claim 14, contamination of an exhaust means is controlled and the fall of exhausting capability can be prevented.
[0296]Since the vaporizer and the reaction chamber are formed by integral construction according to the CVD system for liquid materials of this invention according to claim 15, transportation of the vaporized liquid material to a reaction chamber from a vaporizer is performed efficiently.
[0297]According to the CVD system for liquid materials of this invention according to claim 16, a gas diffusion board is having a feeding hole which passes the vaporized liquid material, and the reactive gas feed holes connected to the supply source of reactive gas, A liquid material and reactive gas can be prevented from blending superfluously, and formation of the resultant by liquid materials other than a predetermined place and mixing of reactive gas can be controlled.
[0298]According to the CVD system for liquid materials of this invention according to claim 17, because susceptor has a lamp heater as a heat source. Since annealing treatment is possible, without taking out a substrate, an oxide film is prevented from being formed in a substrate face, when short-time-ization of annealing treatment is attained and a substrate is taken out.
[0299]According to the CVD system for liquid materials of this invention according to claim 18, degradation of the liquid material by moisture mixing in a liquid material can be prevented by having established the dehydration means into the ingredient container.
[0300]According to the CVD process using the liquid material of this invention according to claim 19, membraneous qualities, such as the electrical property of a BST film, can be improved by adding N_2O as an oxidizer in addition to O_2.
[0301]According to the CVD process using the liquid material of this invention according to claim 20, by forming a BST film gradually and performing predetermined processing to an initial film, the initial film which is easy to make it amorphous can be crystallized, and membraneous qualities, such as the electrical property of a BST film, can be improved.
[0302]As predetermined processing, by performing lamp annealing processing, the initial film which is easy to make it amorphous can be crystallized, and, according to the CVD process using the liquid material of this invention according to claim 21, membraneous qualities, such as the electrical property of a BST film, can be improved after initial film formation.

[0303]According to the CVD process using the liquid material of this invention according to claim 22, membraneous qualities, such as the electrical property of a BST film, can be improved by forming ST film as an initial film.
[0304]After initial film formation, by performing O_3 processing, the initial film which is easy to make it amorphous can be crystallized, and, according to the CVD process using the liquid material of this invention according to claim 23, membraneous qualities, such as the electrical property of a BST film, can be improved.
[0305]After initial film formation, by performing O_2 plasma treatment, the initial film which is easy to make it amorphous can be crystallized, and, according to the CVD process using the liquid material of this invention according to claim 24, membraneous qualities, such as the electrical property of a BST film, can be improved.
[0306]According to the CVD process using the liquid material of this invention according to claim 25, by giving mechanical polish to a substrate, the foreign matter on a substrate can be removed and membraneous qualities, such as an electrical property, can be improved.
[0307]According to the CVD process using the liquid material of this invention according to claim 26, by performing washing processing by HF to a substrate, the foreign matter on a substrate can be removed and membraneous qualities, such as an electrical property, can be improved.
[0308]According to the CVD process using the liquid material of this invention according to claim 27, step coverage nature can improve by low-temperature-izing temperature of a substrate, and a homogeneous film can be formed also in the height direction of a level difference.
[0309]According to the CVD process using the liquid material of this invention according to claim 28, membraneous qualities, such as the electrical property of a BST film, can be improved by supplying supply of the liquid organic metallic compound which is Ti raw material from the liquid material which dissolved the solid state DPM system organic metallic compound in the organic solvent.
[0310]According to the liquid material for the CVD of this invention according to claim 29, the evaporation characteristic of a liquid material can be improved by using the solvent which contains the ligand of an organic metallic compound in the part.
[0311]According to the liquid material for the CVD of this invention according to claim 30, the evaporation characteristic of a liquid material can be improved by having used tetrahydropyran as a solvent.
[0312]According to the liquid material for the CVD of this invention according to claim 31, the evaporation characteristic of a liquid material can be improved by having used dioxane as a solvent.
[0313]According to the liquid material for the CVD of this invention according to claim 32, the evaporation characteristic of a liquid material can be improved by using a nonpolar molecule solvent as a solvent.

CLAIMS

[Claim(s)]
[Claim 1]An ingredient container for accommodating a liquid material which melted a

solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, A CVD system for liquid materials washing inside of said piping by having further a solvent container which accommodates only said solvent liquid, and sending out said solvent to said piping from a solvent container.
[Claim 2]An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, A CVD system for liquid materials having further an inactive gas charging line which supplies inactive gas which raises sending-out speed of said liquid material which is connected to said piping which connects said ingredient container and said vaporizer, and is sent out to said vaporizer from said ingredient container.
[Claim 3]The CVD system for liquid materials according to claim 2 characterized by ****** further provided with an inactive gas cooling method for cooling inactive gas which is attached to said inactive gas charging line, and flows through inside of said inactive gas feed pipe.
[Claim 4]The CVD system for liquid materials according to claim 2 being connected to said inactive gas charging line, having further a solvent container which accommodates only said solvent liquid, and sending out said solvent liquid to said inactive gas charging line.
[Claim 5]An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, A CVD system for liquid materials which was connected to said piping which connects said ingredient container and said vaporizer, was maintained at said vaporizer and power at the same pressure, and was further provided with a receiving container in which only fixed time accommodates said liquid material sent out from said ingredient container.
[Claim 6]A CVD system for liquid materials characterized by comprising the following.
An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, said vaporized liquid material.
In a CVD system which was equipped with a reaction chamber which forms a thin film layer using a reactant gas and to which between said ingredient container, said vaporizer, and said reaction chamber was connected by piping, A regulating valve which adjusts orifice resistance and adjusts a pressure in said piping which connects said ingredient container and said vaporizer near [said] the vaporizer of said piping which connects said

ingredient container and said vaporizer.

[Claim 7]The CVD system for liquid materials according to any one of claims 1 to 6 constituting from piping of said piping which connects said ingredient container and said vaporizer formed by PTFE (Poly Tetra Fluoro Ethylene) in the neighborhood of a vaporizer at least.
[Claim 8]The CVD system for liquid materials according to any one of claims 1 to 6 characterized by establishing a wrap-shaped piping cooling method for said piping near the vaporizer of said piping which connects said ingredient container and said vaporizer.
[Claim 9]Said piping which connects said ingredient container and said vaporizer, and said piping which connects said reaction chamber with said vaporizer so that said liquid material may be given to a forward direction to gravity and said vaporized liquid material may be sent out to an opposite direction to gravity, respectively, The CVD system for liquid materials according to any one of claims 1 to 8 connecting to said vaporizer.
[Claim 10]The CVD system for liquid materials according to any one of claims 1 to 9, wherein an inside of said vaporizer is filled up with a minute metal ball by which the temperature rise was carried out and said liquid material contacts and evaporates in said minute metal ball.
[Claim 11]The CVD system for liquid materials according to any one of claims 1 to 10 having a valve for opening sectional area adjustment to which an effective area product of said piping is changed by adjusting the degree of opening and closing of a valve near [said] the vaporizer of said piping which connects said reaction chamber with said vaporizer.
[Claim 12]By a cooling method provided in a field to which said reaction chamber mixes said vaporized liquid material and said reactant gas, and is provided with a gas diffusion board uniformly diffused in said reaction chamber, and said gas diffusion board of a wall of said reaction chamber contacts. The CVD system for liquid materials according to any one of claims 1 to 11 keeping temperature of said gas diffusion board constant.
[Claim 13]Said reaction chamber lays a substrate with which said thin film layer is formed, is provided with susceptor which heats this substrate, and said susceptor, A heating element used as a heat source, and a conductor which tells heat from said heating element to said substrate by heat conduction, It is provided in the circumference of said heating element, a supporter which accommodates said conductor, and said heating element and said conductor, and Said supporter, The CVD system for liquid materials according to any one of claims 1 to 12 which having a heat-insulating element which insulates said heating element and said conductor, and constituting.
[Claim 14]Equip the exterior of a reaction chamber with an exhaust means for exhausting said vaporized liquid material and said reactant gas, and between said exhaust means and said reaction chamber, The CVD system for liquid materials according to any one of claims 1 to 13 provided with a gas adsorption means to cool, to adsorb said vaporized liquid material and said reactant gas, and to prevent said liquid material and said reactant gas from reaching said exhaust means.
[Claim 15]An ingredient container for accommodating a liquid material which melted a solid material in solvent liquid and was formed in it, a vaporizer which carries out the temperature rise of said liquid material, and makes it evaporate, and said vaporized liquid material, A CVD system for liquid materials which was provided with a reaction chamber

which forms a thin film layer using a reactant gas and with which said vaporizer and said reaction chamber were formed by integral construction.
[Claim 16]A feeding hole which said reaction chamber is provided with a gas diffusion board which diffuses said vaporized liquid material uniformly in said reaction chamber, and said gas diffusion board makes pass said said vaporized liquid material, The CVD system for liquid materials according to claim 15 having the reactive gas feed holes connected to a supply source of said reactive gas.
[Claim 17]The CVD system for liquid materials according to claim 15, wherein said reaction chamber lays a substrate with which said thin film layer is formed, and is provided with susceptor which heats this board and said susceptor has a lamp heater as a heat source.
[Claim 18]The CVD system for liquid materials according to any one of claims 1 to 17 establishing a dehydration means into said ingredient container.
[Claim 19]A vaporizing raw material which made a liquid material which dissolved a solid state DPM system organic metallic compound which are Ba and Sr raw material in an organic solvent heat and evaporate, A thing which made a liquid organic metallic compound which is Ti raw material evaporate is mixed, chemical vapor deposition (Chemical Vapor Deposition : omit the following CVD) which makes it react to O_2 which is an oxidizer, and forms a thin film layer on a substrate -- law () [Ba and] Sr) -- it sets to a CVD process using a liquid material which forms a TiO_3 (it omits the following BST) film -- a CVD process using a liquid material also adding N_2O as an oxidizer in addition to O_2.
[Claim 20]A vaporizing raw material which made a liquid material which dissolved a solid state DPM system organic metallic compound which are Ba and Sr raw material in an organic solvent heat and evaporate, In a CVD process using a liquid material which forms a BST film with a CVD method which mixes a thing which made a liquid organic metallic compound which is Ti raw material evaporate, introduces into a reaction chamber, and carries out a chemical reaction to an oxidizer there, and which is made to vapor-deposit on a substrate, A process of performing predetermined processing to said initial film in order to crystallize said initial film which is easy to make membrane formation of said BST film amorphous with a formation process of an initial film which is a film in early stages of membrane formation, A CVD process using a liquid material considering it as gradual membrane formation performed by dividing into a process of forming a latter-part film on said initial film.
[Claim 21]A CVD process using the liquid material according to claim 20, wherein said predetermined processing performs lamp annealing processing after said initial film formation.
[Claim 22]A CVD process using the liquid material according to claim 20, wherein said predetermined processing forms ST film as said initial film.
[Claim 23]A CVD process using the liquid material according to claim 20, wherein said predetermined processing performs O_3 processing which puts said initial film to O_3 gas after said initial film formation.
[Claim 24]A CVD process using the liquid material according to claim 20, wherein said predetermined processing performs O_2 plasma treatment which puts said initial film to O_2 plasma after said initial film formation.
[Claim 25]A CVD process using the liquid material according to any one of claims 20 to

24 characterized by giving mechanical polish (Chemical Mechanical Polishing) to said substrate in order to remove a foreign matter on said substrate, before forming membranes on said substrate.
[Claim 26]A CVD process using the liquid material according to any one of claims 20 to 24 characterized by performing washing processing by HF (fluoric acid) to said substrate in order to remove a foreign matter on said substrate, before forming membranes on said substrate.
[Claim 27]A CVD process using the liquid material according to any one of claims 20 to 24 having low-temperature-ized temperature of said substrate and raising step coverage nature.
[Claim 28]A CVD process using the liquid material according to any one of claims 20 to 24 supplying supply of a liquid organic metallic compound which is said Ti raw material from a liquid material which dissolved a solid state DPM system organic metallic compound in an organic solvent.
[Claim 29]A liquid material for CVD using a solvent which contains a ligand of this organic metallic compound in the part in a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent.
[Claim 30]A liquid material for CVD using tetrahydropyran as this solvent in a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent.
[Claim 31]A liquid material for CVD using dioxane as this solvent in a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent.
[Claim 32]A liquid material for CVD using a nonpolar molecule solvent as this solvent in a liquid material for CVD made to come to dissolve an organic metallic compound in a solvent.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]It is a figure showing the composition of the CVD system for liquid materials of working example 1 of this invention.
[Drawing 2]It is a figure showing the composition of the CVD system for liquid materials of working example 2 of this invention.
[Drawing 3]It is a figure showing the composition of the CVD system for liquid materials of the modification of working example 2 of this invention.
[Drawing 4]It is a figure showing the composition of the CVD system for liquid materials of working example 3 of this invention.
[Drawing 5]It is a figure showing the composition of the CVD system for liquid materials of working example 4 of this invention.
[Drawing 6]It is a figure showing the composition of the CVD system for liquid materials of working example 5 of this invention.
[Drawing 7]It is a figure showing the composition of the CVD system for liquid materials of working example 6 of this invention.
[Drawing 8]It is a figure showing the composition of the CVD system for liquid materials of working example 7 of this invention.

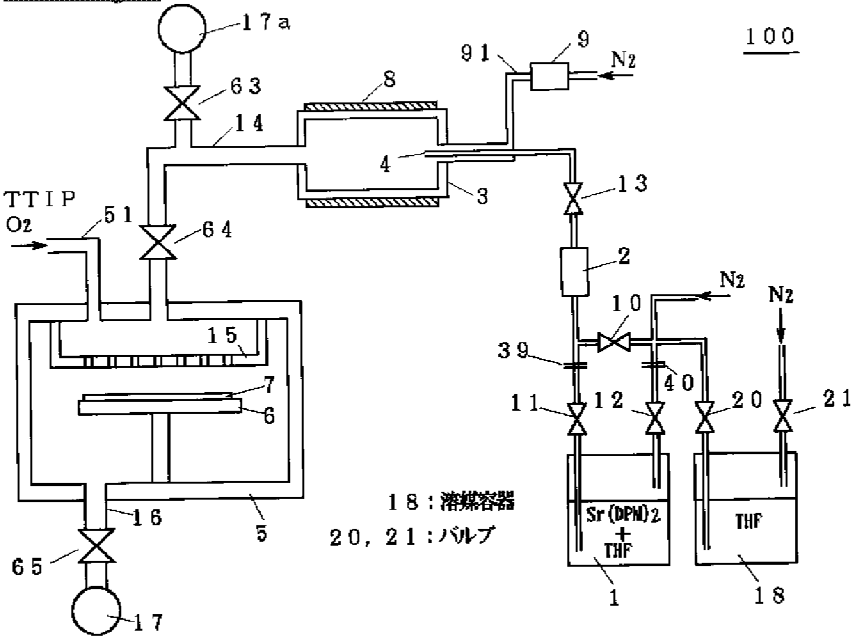
[Drawing 9]It is a figure showing the composition of the CVD system for liquid materials of working example 8 of this invention.
[Drawing 10]It is a figure showing the composition of the CVD system for liquid materials of working example 9 of this invention.
[Drawing 11]It is a figure showing the composition of the CVD system for liquid materials of working example 10 of this invention.
[Drawing 12]It is a figure showing the composition of the CVD system for liquid materials of working example 11 of this invention.
[Drawing 13]It is a part drawing of the CVD system for liquid materials of working example 11 of this invention.
[Drawing 14]It is a figure showing the composition of the CVD system for liquid materials of working example 12 of this invention.
[Drawing 15]It is a figure showing the composition of the CVD system for liquid materials of working example 13 of this invention.
[Drawing 16]It is a part drawing of the CVD system for liquid materials of working example 14 of this invention.
[Drawing 17]It is a sectional view of the film formed of the CVD process using the liquid material of working example 15 of this invention.
[Drawing 18]It is a sectional view of the film formed of the CVD process using the liquid material of working example 16 of this invention.
[Drawing 19]It is a sectional view of the film formed of the CVD process using the liquid material of working example 17 of this invention.
[Drawing 20]It is a sectional view of the film formed of the CVD process using the liquid material of working example 18 of this invention.
[Drawing 21]It is a sectional view of the film formed of the CVD process using the liquid material of working example 19 of this invention.
[Drawing 22]It is a sectional view of the film formed of the CVD process using the liquid material of working example 20 of this invention.
[Drawing 23]It is a sectional view of the film formed of the CVD process using the liquid material of working example 21 of this invention.
[Drawing 24]It is a sectional view of the film formed of the CVD process using the liquid material of working example 22 of this invention.
[Drawing 25]It is a sectional view of the film formed of the CVD process using the liquid material of working example 23 of this invention.
[Drawing 26]It is a sectional view of the film formed of the CVD process using the liquid material of working example 24 of this invention.
[Drawing 27]It is a figure showing the composition of the conventional CVD system for liquid materials.
[Drawing 28]It is a figure showing the composition of the conventional CVD system for liquid materials.
[Drawing 29]It is a sectional view of the film formed of the CVD process using the conventional liquid material.
[Drawing 30]It is a sectional view of the film formed of the CVD process using the conventional liquid material.
[Description of Notations]
1b, 101, and 101a Liquid material container

3b and 103 Vaporizer
4a, 4b, 104 spraying nozzles
8b Heater
14a, 14b vaporized gas feed pipe
5a and 105 Reaction chamber
6a Heating stage
11a, 11b, 12a, 12b, 13a, 13b, 20, and 21 Valve
15a, a 115 gas-diffusion board
15 s Buck
15 h Diffusion mouth
17, 17b, 117 vacuum pumps
18 Solvent container
18b Solvent container
23 The heat exchanger for cooling
24 Massflow controller
25 Liquid pool tank
26 Valve
27 Teflon small tube
28 Water cooled jacket
29 Needle valve
30 Conductance valve
31 Opening and closing plate
32 Driving shaft
33 Driving source
34 Pressure gauge
35 Minute metal ball
36 Discharge valve
37 Introduction valve
39a, 39b, 40a, and 40b Terminal area
41 Heater
42 Susceptor
43 Heater cover
44 The passage for cooling
45 Heat-insulating element
47 The heat exchanger for cooling
48 Cold trap
51 Resultant
52 Gas material
53 Condensation object
60, 61, 36c, and 40c Terminal area
82 Sealant
83 Fixing screw
84 Liquid material
85 Dehydrator
86 Container lid
87 Package body

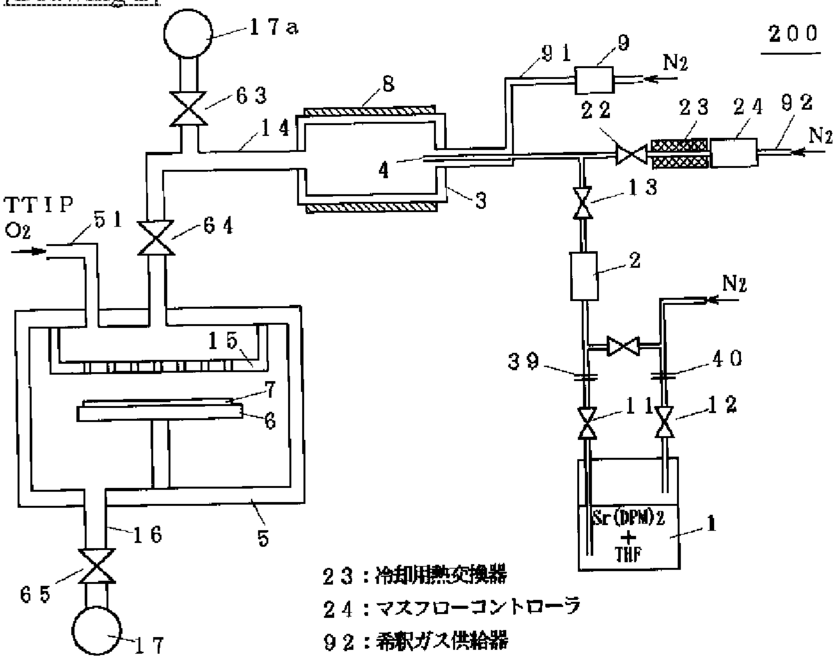
P11 and P12 Piping
91a Dilution gas feed pipe
92 Dilution gas feeder
102 Liquid supply means
107 Film formation substrate
109 and 124 Massflow controller
110, 111, 112, 113, and 122 Valve
138 Cooler style
146 Gate valve
154 The 1st current plate
155 The 2nd current plate
156 Material gas diffusion mouth
157 Oxidizing gas diffusion mouth
158 Oxidizing gas feed pipe
159 Infrared lamp heater
160 Light reflector
161 Reaction chamber heating heater
190 Support plate
The BST film which added and formed L4 N_2O
L5 Initial film of BST which performed lamp annealing processing
L6 Latter-part BST film
The initial film of BST which performed L7 O_3 processing
The initial film of BST which performed L9 O_2 plasma treatment
The initial film of BST which increased and formed the L10 O_2 flow
L11 Initial film of BST which changed and formed composition ratio
L12 Initial film of BST which decreased in number and formed membrane formation speed
L13 ST film
L17 Initial film of BST obtained by low temperature-ization

DRAWINGS

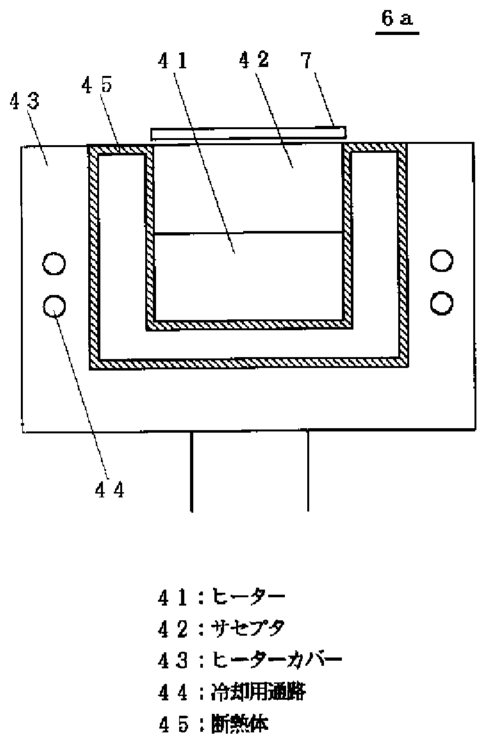
[Drawing 1]



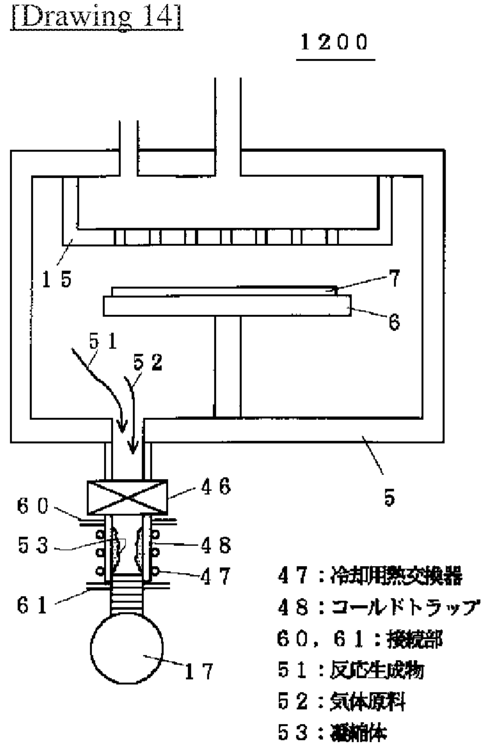
[Drawing 2]



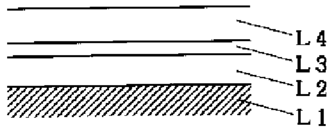
[Drawing 13]



[Drawing 14]

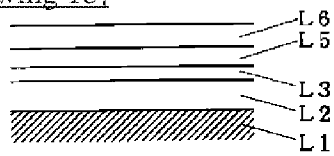


[Drawing 17]



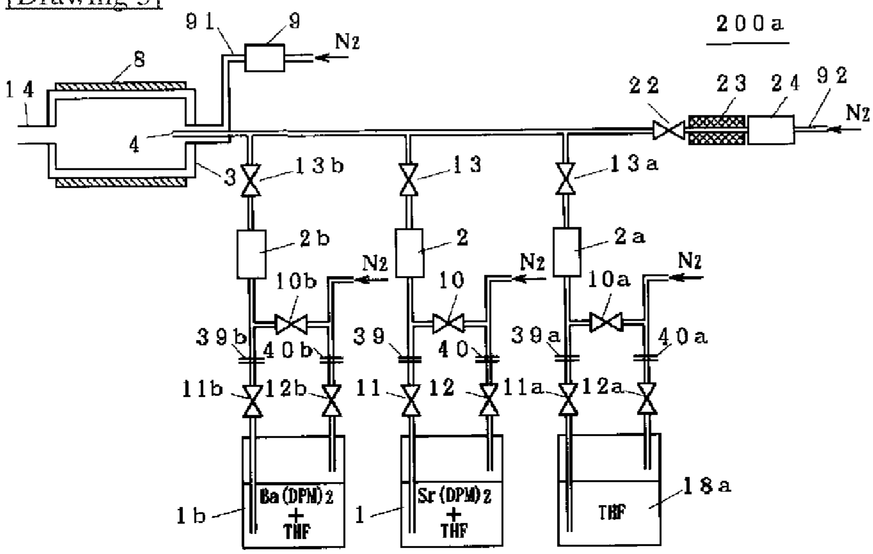
L４：N_2Oを添加して形成したＢＳＴ膜

[Drawing 18]



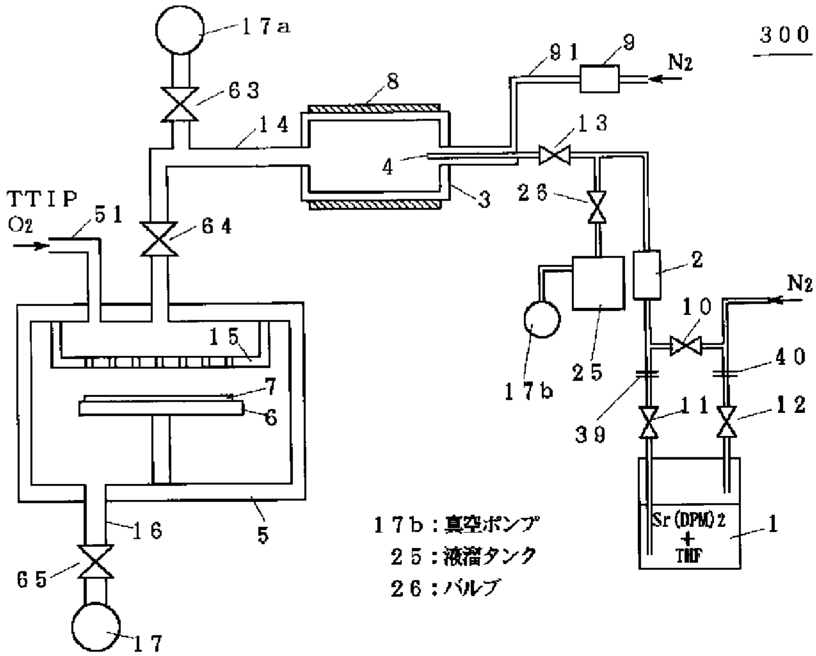
L５：ランプアニール処理を施したＢＳＴ初期膜
L６：後段ＢＳＴ膜

[Drawing 3]

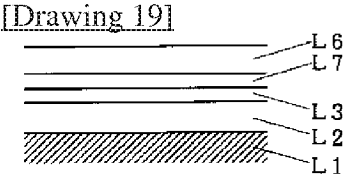


1b：液体原料容器　　39a，39b，40a，40b：接続部
18a：溶媒容器　　11a，11b，12a，12b，13a，13b：バルブ

[Drawing 4]

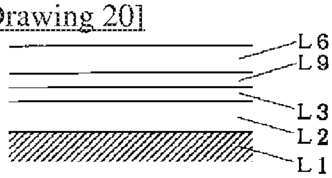


[Drawing 19]



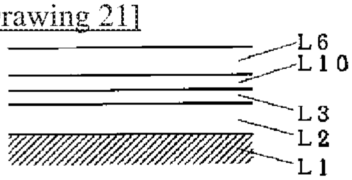
Ｌ７：O_3処理を施したＢＳＴ初期膜

[Drawing 20]



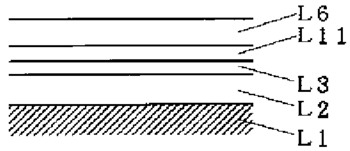
Ｌ９：O_2プラズマ処理を施したＢＳＴ初期膜

[Drawing 21]



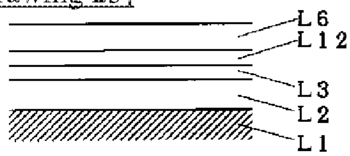
Ｌ１０：O_2流量を増加して形成したＢＳＴ初期膜

[Drawing 22]



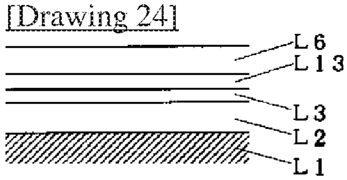
Ｌ１１：組成比を変更して形成したＢＳＴ初期膜

[Drawing 23]



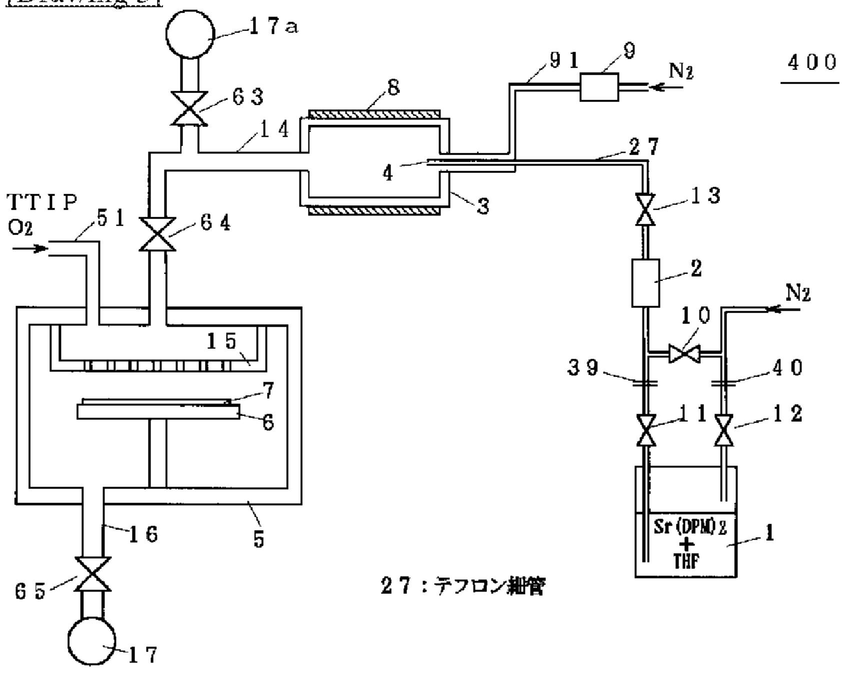
Ｌ１２：成膜速度を減少して形成したＢＳＴ初期膜

[Drawing 24]



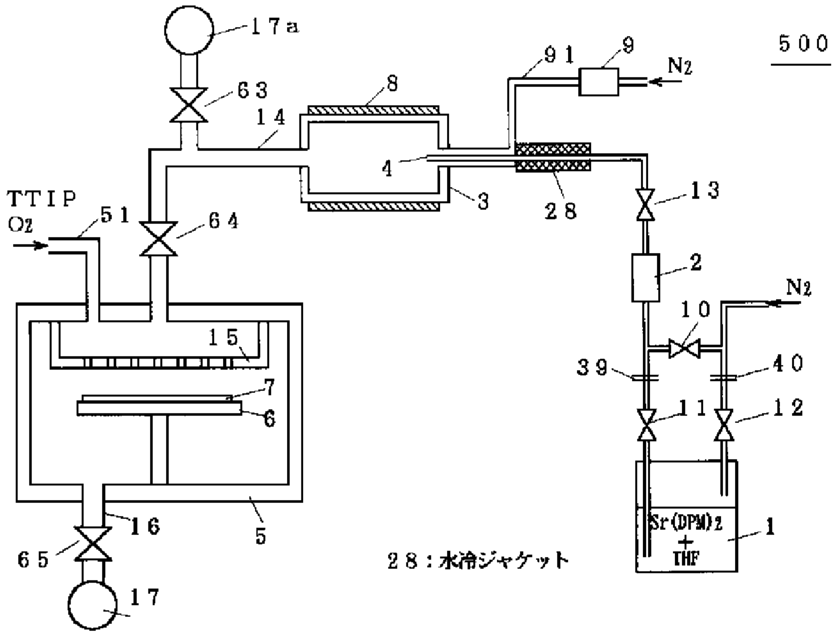
Ｌ１３：ＳＴ膜

[Drawing 5]

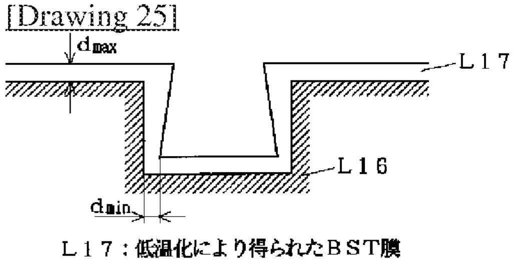


２７：テフロン細管

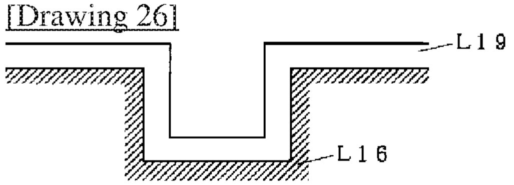
[Drawing 6]



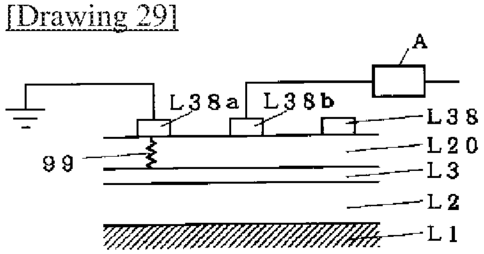
[Drawing 25]



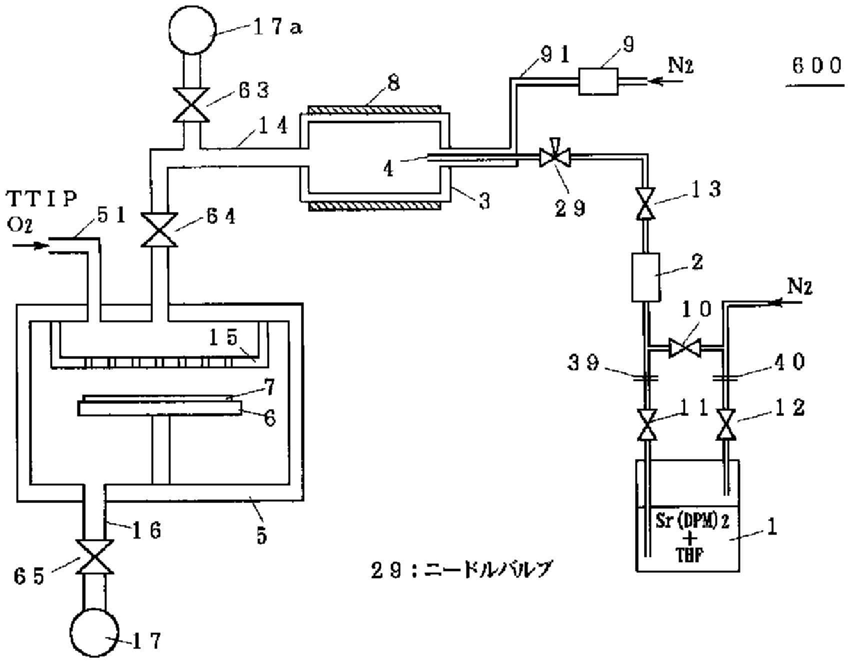
[Drawing 26]



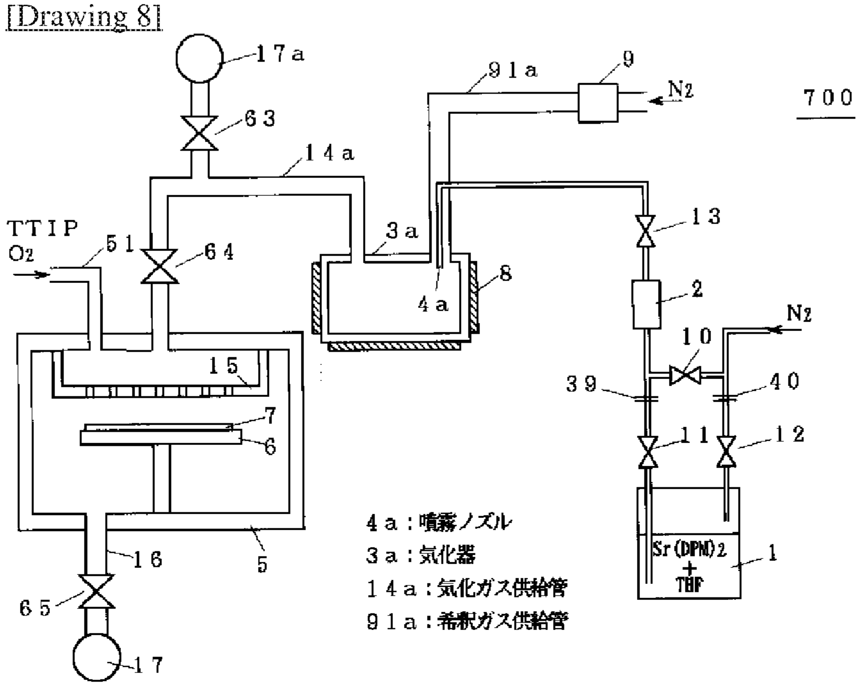
[Drawing 29]



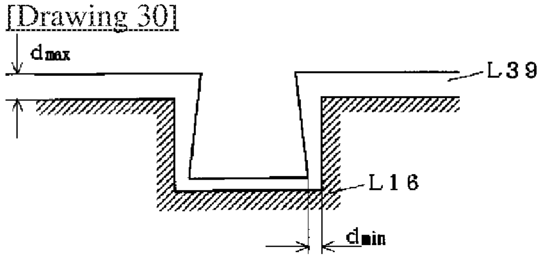
[Drawing 7]



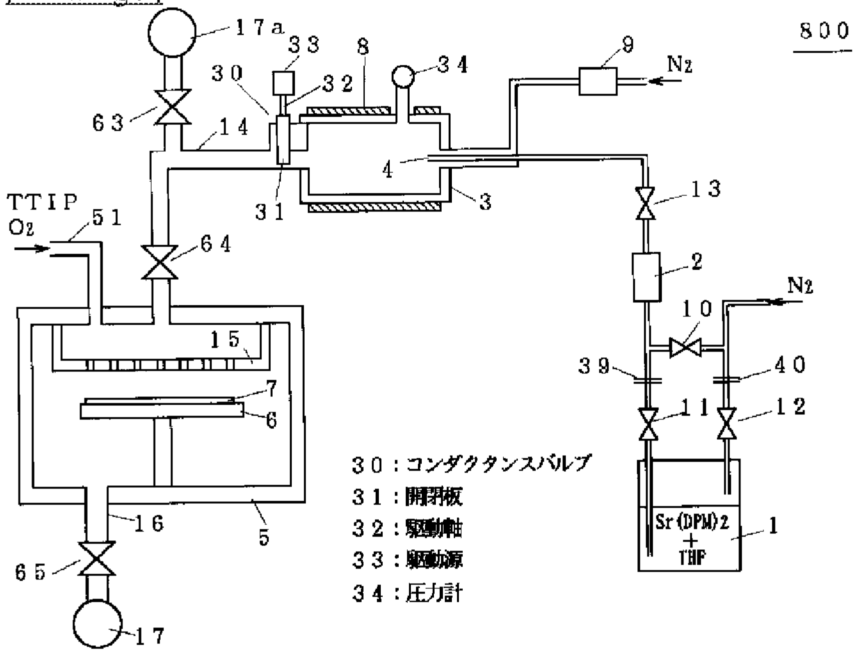
[Drawing 8]



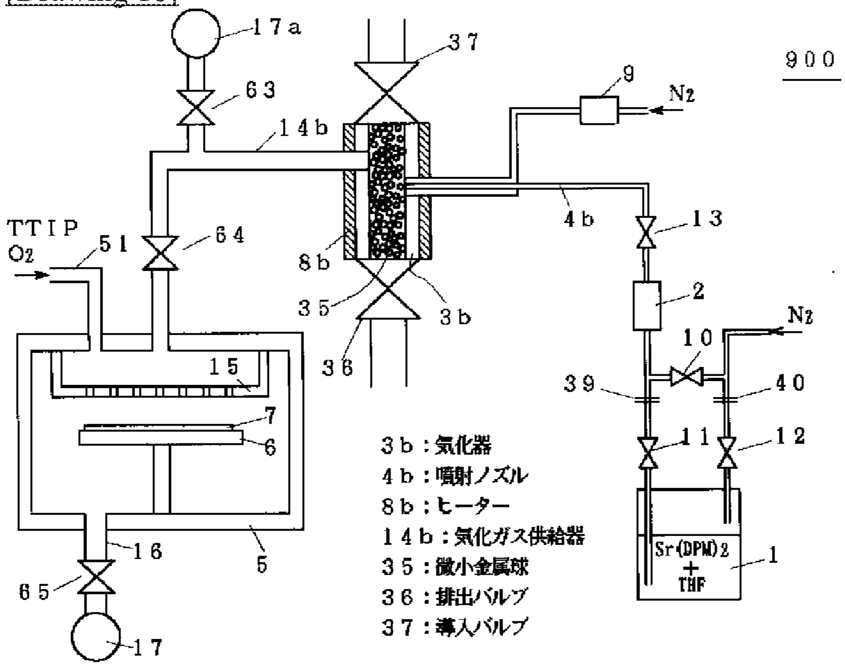
[Drawing 30]



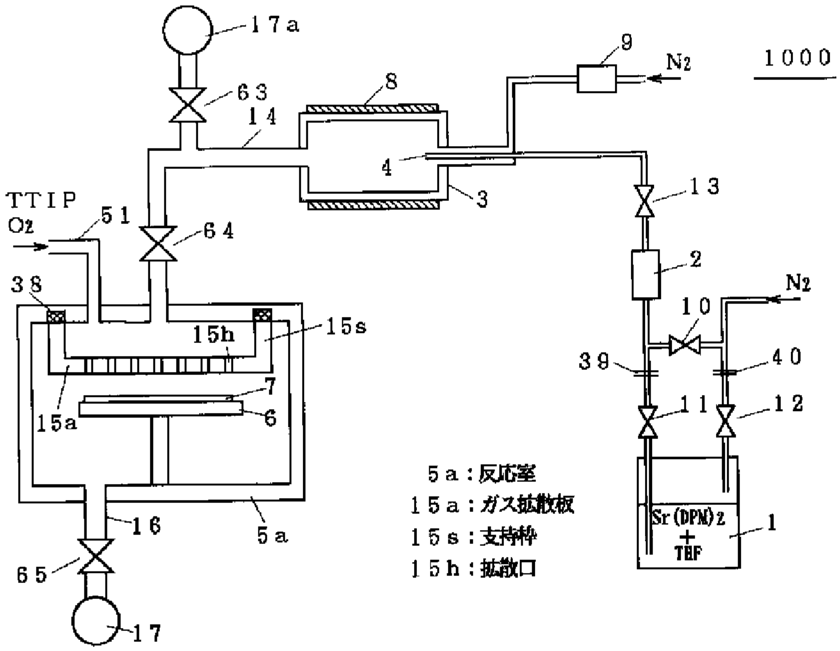
[Drawing 9]



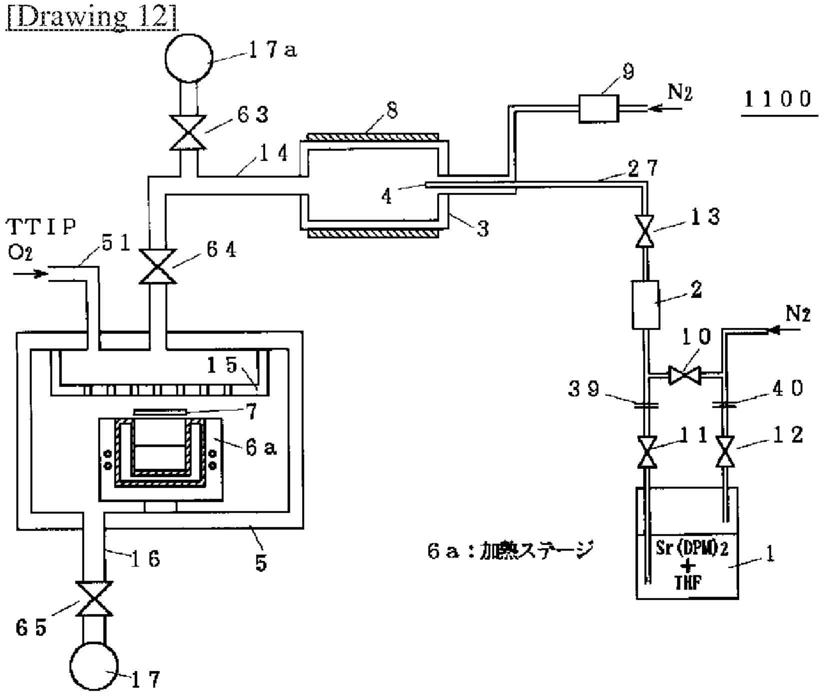
[Drawing 10]



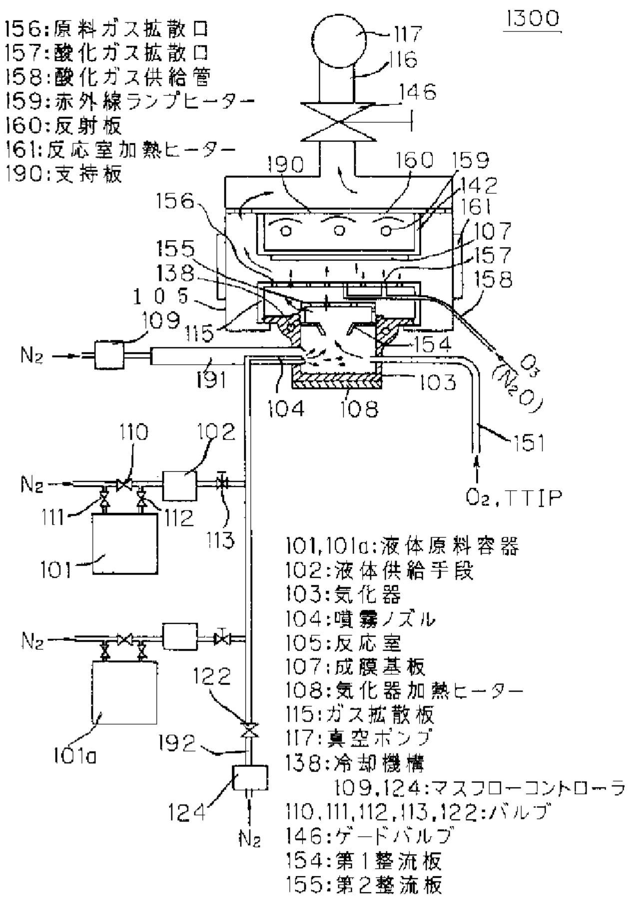
[Drawing 11]



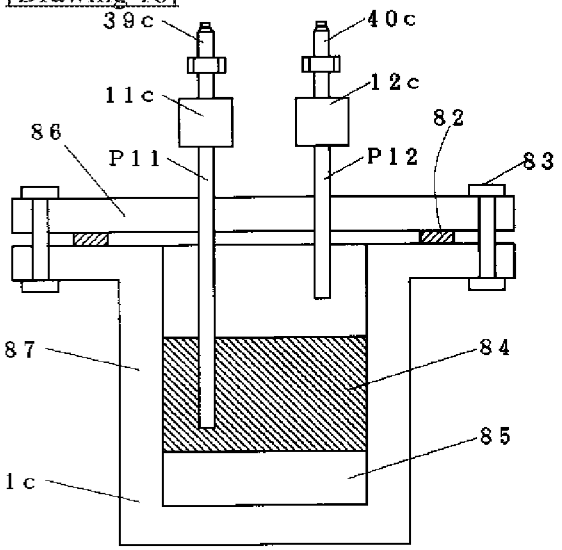
[Drawing 12]



[Drawing 15]



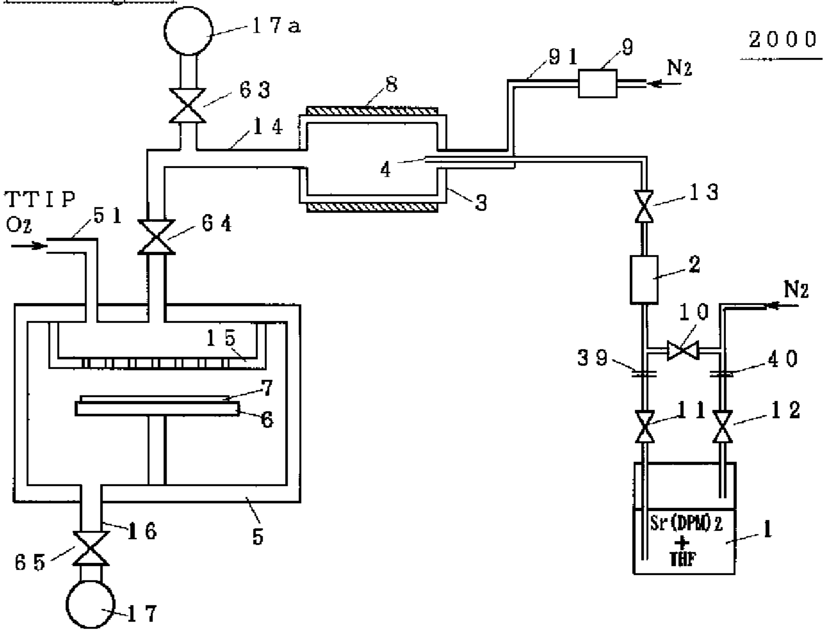
[Drawing 16]



82：シール材
83：固定ネジ
84：液体原料
85：脱水剤
86：容器蓋
87：容器本体

11c，12c：バルブ
36c，40c：接続部
P11，P12：配管

[Drawing 27]



[Drawing 28]